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The document serves as a text to state agencies in the development of their gaseous fluoride emission regulations from existing phosphate fertilizer plants. Recommended emission units are suggested for five production facilities: wet-process phosphoric acid, diammonium phosphate, superphosphoric acid, triple superphosphate, granular triple superphosphate production and storage. Information contained within includes data on the phosphate fertilizer industry and control technology, a discussion of the guideline emission limitations and the supporting data, and analyses of the environmental and economic impacts of the guideline limits.

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Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park. North Carolina 27711

March 1977

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This document does not constitute a general endorsement of supplementary control systems as a control alternative. It is intended only to assist the responsible control agencies in those limited situations where legislation, EPA or the courts permit its use.

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1. INTRODUCTION AND SUMMARY

1.1 INTRODUCTION

Section 111(d) of the Clean Air Act, 42 U.S.C. 1857c-6(d), as amended, requires EPA to establish procedures under which States submit plans to control certain existing sources of certain pollutants. On November 17, 1975 (40 FR 53340), EPA implemented section 111(d) by promulgating Subpart B of 40 CFR Part 60, establishing procedures and requirements for adoption and submittal of State plans for control of "designated pollutants" from "designated facilities." Designated pollutants are pollutants which are not included on a list published under section 108(a) of the Act (National Ambient Air Quality Standards) or section 112(b)(1)(A) (Hazardous Air Pollutants), but for which standards of performance for new sources have been established under section 111(b). A designated facility is an existing facility which emits a designated pollutant and which would be subject to a standard of performance for that pollutant if the existing facility were new.

Standards of performance for five categories of new sources in the phosphate fertilizer industry were promulgated in the FEDERAL REGISTER (40 FR 33152) on August 6, 1975, to be incorporated into the Code of Federal Regulations under 40 CFR Part 60. New subparts T, U, V, W, and X were added to set standards of performance for fluoride emissions from new plants manufacturing wet-process phosphoric acid (WPPA), superphosphoric acid (SPA), diammonium phosphate (DAP), triple superphosphate (TSP), and for storage facilities used in the manufacture of granular triple superphosphate (GTSP). The States, therefore, are required to adopt fluoride emission standards for existing phosphate fertilizer plants which would be subject to the standards of performance if they were new.

Subpart B of 40 CFR Part 60 provides that EPA will publish a guideline document for development of State emission standards after promulgation of any standard of performance for a designated pollutant. The document will specify emission guidelines and times for compliance and will include other pertinent information, such as discussion of the pollutant's effects on public health and welfare and a description of control techniques and their effectiveness and costs. The emission guidelines will reflect the degree of emission reduction attainable with the best adequately demonstrated systems of emission reduction, considering costs, as applied to existing facilities.

After publication of a final guideline document for the pollutant in question, the States will have nine months to develop and submit plans for control of that pollutant from designated facilities. Within four months after the date for submission of plans, the Administrator will approve or disapprove each plan (or portions thereof). If a state plan (or portion thereof) is disapproved, the Administrator will promulgate a plan (or portion thereof) within six months after the date for plan submission. These and related provisions of subpart B are basically patterned after section 110 of the Act and 40 CFR Part 51 (concerning adoption and submittal of state implementation plans under section 110).

As discussed in the preamble to subpart B, a distinction is drawn between designated pollutants which may cause or contribute to endangerment of public health (referred to as "health-related pollutants") and those for which adverse effects on public health have not been demonstrated (referred to as "welfare-related pollutants"). For health-related pollutants, emission standards and compliance times in state plans must ordinarily be at least as stringent as the corresponding emission guidelines and compliance times in EPA's guideline documents. As provided in Subpart B, States may apply less stringent requirements for particular facilities or classes of facilities when economic factors or physical limitations make such application significantly more reasonable.

For welfare-related pollutants, States may balance the emission guidelines, times for compliance, and other information provided in a guideline document against other factors of public concern in establishing emission standards, compliance schedules, and variances, provided that appropriate consideration is given to the information presented in the guideline document and at public hearing(s) required by subpart B and that all other requirements of subpart B are met. Where sources of pollutants that cause only adverse effects to crops are located in non-agricultural areas, for example, or where residents of a community depend on an economically marginal plant for their livelihood, such factors may be taken into account (in addition to those that would justify variances if a health-related pollutant were involved). Thus, States will have substantial flexibility to consider factors other than technology and cost in establishing plans for the control of welfare-related pollutants if they wish.

For reasons discussed in section 2 of this document, the Administrator has determined that fluoride emissions from phosphate fertilizer plants may cause or contribute to endangerment of the public welfare but that adverse effects on public health have not been demonstrated. As discussed above, this means that fluoride emissions from phosphate fertilizer plants will be considered a welfare-related pollutant and the States will have greater flexibility in establishing plans for the control of fluorides than would be the case if public health might be affected.

This guideline document provides a brief description of the phosphate fertilizer industry, the five manufacturing categories for which fluoride emission guidelines are established, and the nature and source of fluoride emissions. Also, information is provided regarding the effects of airborne fluorides on health, crops, and animals.

Emphasis has been placed on the technical and economic evaluation of control techniques that are effective in reducing particulate and gaseous fluoride emissions, with particular emphasis on retrofitting existing plants. Some costs were seldomly available and were fragmentary. Therefore, the cost basis for adoption of State standards based on the emission guidelines is instead developed by engineering cost estimates on a hypothetical phosphate fertilizer plant complex where assumed mediocre controls are replaced with controls based on the emission guidelines. These retrofits are called retrofit models and are presented in Section 6.1.3.1.

The emission guidelines and the control equipment on which they are based are discussed in Sections 7 and 8. The environmental assessment of the emission guidelines is presented and discussed in Section 9. The remainder of this introductory section summarizes information presented in subsequent sections.

1.2 HEALTH AND WELFARE EFFECTS OF FLUORIDES

Fluoride emissions from phosphate fertilizer plants have been determined to be welfare-related [i.e. no demonstrated impact upon public health for purposes of section 111(d)]. The daily intake of fluoride inhaled from the ambient air is only a few hundredths of a milligram - a very small fraction of the total intake of the average person. If a person is exposed to ambient air containing about eight micrograms (μg) of fluoride per cubic meter, which is the maximum average concentration that is projected in the vicinity of a fertilizer facility with only moderate control equipment (Table 9-5), his total daily intake from this source is calculated to be about 150 μg. This is very low when compared with the estimated daily intake of about 1200 μg from food, water and other sources for the average person. Also, the intake of fluoride indirectly through standard food chains is insignificant. Fluorides are not passed into dairy products and are only found in farm produce in very small amounts.

Fluorides do, however, cause damage to livestock and vegetation in the immediate vicinity of fertilizer plants. Ingestion of fluorides by livestock from hay and forage causes bone lesions, lameness and impairment of appetite that can result in decreased weight gain or diminished milk yield. It can also affect developing teeth in young animals, causing more or less severe abnormalities in permanent teeth. Exposure of plants to atmospheric fluorides can result in accumulation, foliar lesions, and alteration in plant development, growth, and yield.

1.3 FLUORIDES AND THEIR CONTROL

For purposes of standards of performance for new stationary sources (SPNSS) and the attendant requirements of section 111(d), emissions of "total fluorides," rather than specific fluorides are limited. Total fluorides means molecular fluorine and all compounds of fluorine measured by reference methods identified in subparts T, U, V, W, and X and specified in Appendix A of 40 CFR, Part 60, or by equivalent or alternative test methods.

Good control of fluoride emissions from phosphate fertilizer manufacturing operations is achievable by water scrubbers which are properly designed, operated, and maintained. The most satisfactory scrubber for general use is the spray crossflow packed scrubber. Other scrubbers, such as the venturi and the cyclonic spray tower can give satisfactory results when used in series. The spray-crossflow packed scrubber, shown diagramatically in Figure 6-1, owes much of its success to its greater fluoride absorption capability and its relative freedom from solids plugging. This plugging has given some trouble in the past in DAP and GTSP plants, but current designs are available which have acceptable turnaround periods[1]. One design involves a venturi ahead of, and integral with, the scrubber.

A description of the performance of water scrubbers in fluoride emission control is given in Table 1-1. The industry-wide range of control is given by a variety of scrubbers and is discussed in Chapter

6. The scrubber data associated with best control technology were obtained from EPA sponsored tests conducted during the development of SPNSS. Most of the scrubbers tested were the spray crossflow packed type, but a few venturi were tested.

1.4 EMISSION GUIDELINES

Emission guidelines for existing phosphate fertilizer manufacturing facilities for control of fluoride emissions are described in this Section. Table 1-2 gives the fluoride emission levels that may be achieved by application of best adequately demonstrated technology to existing facilities, including five manufacturing processes and the storage facilities for granular triple superphosphate. Comparison of these emission guidelines with the ranges shown for well-controlled plants (Table 1-1) shows that equivalent control of fluoride emissions can be achieved by application of best adequately demonstrated technology for either new or existing sources.

Adoption of these controls would result in fluoride emission reductions ranging from about 50 percent for granular triple superphosphate (GTSP) production facilities to around 90 percent for run-of-pile triple superphosphate (ROP-TSP) plants. Overall nationwide emissions would be reduced by about 75 percent.

The emission levels of Table 1-2 are identical to the standards of performance for new stationary sources (SPNSS) since the best adequately demonstrated technology applicable is the same type of control equipment. The justification for application of this equipment to existing as well as new sources is summarized in Section 1.6.1 and discussed more completely in Section 8. (Note that all units expressed as "tons" are defined as short tons.)

TABLE 1-1 PERFORMANCE OF AQUEOUS SCRUBBER EMISSION CONTROL EQUIPMENT - IN PHOSPHATE FERTILIZER MANUFACTURING PLANTS.

Fluoride Source	Fluoride Emissions from Control Equipment	
	g TF/kg of P_2O_5 input	
	Industry-Wide Range	Best-Controlled New Plant Segment
Wet-Process Phosphoric Acid	0.01 - 0.30	0.001 - 0.0095
Superphosphoric Acid		
Submerged Combustion	0.06	
Vacuum Evaporation	2.5×10^{-3}	$2.05 \times 10^{-4} - 7.5 \times 10^{-4}$
Diammonium Phosphate	0.03 - 0.25	0.0125 - 0.03
Triple Superphosphate (run-of-pile - ROP)	0.10 - 0.30	0.015 - 0.1505
Granular Triple Superphosphate	0.10 - 0.30	0.02 - 0.135
Granular Triple Superphosphate Storage	$2.5 \times 10^{-4} - 7.5 \times 10^{-4}$*	$0.25 \times 10^{-4} - 2.75 \times 10^{-4}$

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*Units are g TF/hr/kg of P_2O_5 stored.

TABLE 1-2 FLUORIDE EMISSION GUIDELINES FOR EXISTING PHOSPHATE FERTILIZER MANUFACTURING PLANTS.

Process Source of Fluorides	Emission Guidelines	
	Total Fluorides - weight per unit of P_2O_5 input	
	g/kg	lbs/ton
Wet-Process Phosphoric Acid	0.01	0.02
Superphosphoric Acid	0.005	0.01
Diammonium Phosphate	0.03	0.06
Triple Superphosphate (ROP)	0.1	0.2
Granular Triple Superphosphate	0.1	0.2
	g/hr kilogram	lbs/hr ton*
Granular Triple Superphosphate Storage	2.5×10^{-4}	5×10^{-4}

*These denominator units are in terms of P_2O_5 stored.

1.5 COMPLIANCE TIMES

The compliance times for installation of a wet scrubber are given in Table 1-3, which is derived from Figure 6-17. Milestones in the compliance schedule are also shown. The first milestone can increase to 18 weeks if justifiable source tests must be run and control alternatives evaluated. This is rather unlikely, since the spray-crossflow packed scrubber is the one most widely specified for new controls. The interval between milestones two and three is that required for fabrication and shipping. The fabrication time is virtually beyond the control of either the customer or the air pollution control official. For this reason, a range of elapsed time must be understood for fabrication. The compliance time can exceed 78 weeks and depends upon availability of materials of construction, labor factors, work backlogs, and many other things. If a given fertilizer complex has to install several scrubbers, the total time for compliance may exceed

TABLE 1-3

COMPLIANCE TIMES FOR INSTALLATION OF WET SCRUBBER FOR A WET PROCESS PHOSPHORIC ACID PLANT

Milestone	Elapsed Time, Weeks
Submit final control plan to Agency	6
Award scrubber contract	26
Initiate scrubber installation	52
Complete scrubber installation	72
Final compliance achieved	78

that for only one scrubber. In practice, enforcement officials should try to consider each plant on a case-by-case basis and should require proof for the time requirements claimed for each milestone.

1.6 ASSESSMENTS

1.6.1 Economic

The information shown in Table 1-4 provides a major portion of the justification for the emission guidelines. The costs in the table were derived from retrofit models (section 6.1.3.1). The capital and annualized costs shown in Table 1-4 represent emission controls for each separate process.

Actual total expenditures for emission controls of a process have to take into account the control costs allocated to its feed materials. Table 1-5 summarizes retrofit control costs for fertilizer plants of the capacities shown. These costs (see Table 7-1) include prorated WPPA plant control costs according to the amount of acid used. For example, the ROP plant control cost includes the control cost for the 330 tons/day of wet process phosphoric acid required to make 550 TPD of ROP, both on a P_2O_5 basis. Therefore, the annualized control costs, as a percent of sales, differ from those shown in Table 1-4, except for the WPPA plant taken alone. The greatest unit basis cost is for the combination of processing and storage of GTSP. About 75 percent of GTSP production is believed to be already sufficiently controlled while five of eight storage facilities may need to be retrofitted if the States establish emission standards as stringent as the emission guidelines. This would not have a great effect on GTSP manufacture. About 60 percent of DAP plants would

TABLE 1-4 ECONOMIC ASSESSMENT OF FLUORIDE EMISSION GUIDELINES FOR EXISTING PHOSPHATE FERTILIZER MANUFACTURING FACILITIES.*

Process Source of Fluorides	Annualized Control Cost % of Sales	Capital Control Cost of Equipment** $/Annual ton of P_2O_5	Percent of Plants Not Meeting This Emission Guidelines	Applicable Emission Guideline grams/kilogram P_2O_5 input
Wet-Process Phosphoric Acid	.19 - .23	1.39 - 1.65	47	0.01
Superphosphoric Acid	.14	1.15	21	0.005
Diammonium Phosphate	.37	4.44	60	0.03
Triple Super-Phosphate (ROP)	.43-.74	4.42 - 7.59	40	0.1
Granular Triple Superphosphate	.48	5.07	25	0.1
Granular Triple Superphosphate Storage	.42	4.52	70	2.5×10^{-4}***

* Derived from EPA retrofit models at 1974 prices and costs.

** Based upon total annual production at capacity for 330 days/year.

*** Units are grams F/hr/kilogram of P_2O_5 stored. This facility is assumed to accompany a 400 short ton P_2O_5/day GTSP plant.

TABLE 1-5

SUMMARY OF RETROFIT CONTROL COST REQUIREMENTS FOR VARIOUS PHOSPHATE FERTILIZER MANUFACTURING PROCESSES*

End Product	Phosphoric Acid	Superphosphoric Acid	DAP	ROP-TSP	GTSP
Design Rate, tons/day (P_2O_5 Basis)	500	300	500	550	400
Capital Control Cost, \$/annual ton P_2O_5	1.39 - 1.65	2.67	5.96	5.33 - 8.50	10.50
Sales Price (\$ per ton product)	105	152	145	126	130
Annualized Costs					
Unit Basis (\$ per ton product)	.20 - .24	.52	.73	0.66 - 1.05	1.29
As a % of Sales Price	0.2	0.3	0.5	0.5 - 0.8	1.0

*Costs and prices are at 1974 levels

possibly need to be retrofitted. Although this segment of the industry requires the most control effort, control costs are only 0.5 percent of sales.

The capital retrofit costs shown in Table 1-5, while significant, are moderate. Annualized costs as a percent of sales are small, showing that all the control costs can be readily recovered.

Cyclonic spray and venturi scrubbers, alone, do not have more than about two transfer units, whereas the spray-crossflow packed scrubber (SCPS) is furnished in the 5-9 transfer unit range. The former controls would require two or more scrubbers in series to achieve the performance of one spray-crossflow packed scrubber. This scrubber multiplication would cost more in comparison to the SCPS and would not be selected for high degrees of fluoride removal when costs are taken into account. Having made this choice, there is no reason to design short of the SPNSS. A SCPS being designed to achieve 0.08 lbs F/ton for DAP can achieve 0.06 lbs TF/ton if designed with a little additional packing. Therefore, the fluoride emission guidelines given in Table 1-1 reflect the performance of a control system which is judged to be the best when costs are taken into account, and they are identical to the SPNSS.

If the States establish emission standards as stringent as the emission guidelines, the financial impact upon most existing plants will be moderate, as shown in Tables 1-4 and 1-5. The only plants likely to be financially burdened will be: small plants of less than about 170,000 tons per year capacity; plants that are 20 years or more of age; and plants isolated from raw materials, i.e. certain DAP plants that purchase merchant phosphoric acid and ammonia.

1.6.2 Environmental

The environmental assessment provided here is an assessment of the difference between two degrees of control: 1) the reduction in fluoride emissions resulting from application of the emission guidelines and 2) the normal reduction in fluoride emissions resulting from State Implementation Plans (SIP), local regulations, etc.

The adoption of fluoride emission standards would have a beneficial impact upon air quality. Installation of retrofit controls similar to those described in section 6.1.3.1 can reduce fluoride emissions from existing sources by amounts ranging from 50 percent for GTSP to 88 percent for ROP-TSP plants. The projected average nationwide emission reduction that would result from application of the emission guidelines is 73 percent or 1070 tons F/year. The method of deriving these results is described in section 9.1.1.

The removal of fluoride pollutants from fertilizer plant emissions would have a beneficial effect on the environment. The threshold average concentration of fluoride in foliage that results in harmful effects to animals when ingested is 40 ppm. The available data suggest that a threshold for plant deterioration (foliar necrosis) on sensitive plant species is also 40 ppm. As discussed in detail in Chapter 2, an accumulation of fluoride in foliage of more than 40 ppm would result from exposure to a 30 day average air concentration of gaseous fluoride of about 0.5 micrograms per cubic meter ($\mu g/m^3$). In order to evaluate potential ambient concentrations of fluoride, atmospheric dispersion estimates were made for a typical phosphate fertilizer complex. Groundlevel fluoride concentrations were compared for mediocre controls and for controls essentially similar to the emission guidelines shown in Table 1-2. At a distance of about 2.5 kilometers (Table 9-5) from the complex, the 30-day average fluoride ground-level concentration was 3.5 $\mu g/m^3$ for the mediocre controls, and it was 0.5 $\mu g/m^3$ for the good retrofit controls. The conclusion is apparent that for protection of public welfare (i.e. foliage, animals, etc.) mediocre controls are effective for protection of property beyond 15 km (9.3 miles) and best controls are effective beyond 2.5 km (1.5 miles) relative to the fertilizer facility location.

Increased or decreased control of fluorides would not change the volume of aqueous waste generated in a phosphate fertilizer complex. Gypsum pond water is used and re-used, and a discharge is needed only when there is rainfall in excess of evaporation.

Any solid waste generated by scrubbing fluorides would be in the form of fluorosilicates of CaF_2 in the gypsum ponds. Section 9.1.3 shows that the increase in solids discharged to the gypsum pond due to scrubbing in a WPPA plant is only about 0.06 weight percent, a negligible amount. The total fluoride solids increase from a fertilizer complex to the gypsum pond would be nearer four percent of the gypsum discharge, but much of this is from sources other than scrubbing and certainly cannot be charged to small increments in emission standards.

1.6.3 Energy

Energy requirements for State controls based on the emission guidelines, in excess of existing controls, would be small and varying from 0.4 to 25 KWH per ton P_2O_5, depending on the process. Raising the allowable emission levels would have only a small effect on these power figures. Section 9.1.4 estimates the total incremental energy demand for the phosphate fertilizer industry. This total incremental electrical energy demand that would result from installation of retrofit controls to meet State standards based on the guidelines is estimated as 27 x 10^6 KWH/yr, which is energy enough to operate one SPA plant of 300 tons/day P_2O_5 for 115 days/year. Although this energy number can be only an approximation, it puts the incremental energy demand into perspective and shows that it is very small compared to the total annual energy demand for the industry.

1.6.4 Inflation

The costs associated with the emission guidelines for existing phosphate fertilizer plants have been judged not to be of such magnitude to require analysis of the inflationary impact. Screening criteria have been developed by EPA to be used in the impact analysis. These criteria have been outlined in an Agency publication and include:

(1) National annualized cost of compliance.

(2) Total added production cost in relation to sales price.

(3) Net national energy consumption increase.

(4) Added demands or decreased supplies of selected materials.

Should any of the guideline values listed under these criteria be exceeded, a full inflationary impact assessment is required.

1.7 REFERENCES

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2. HEALTH AND WELFARE EFFECTS OF FLUORIDES

2.1 INTRODUCTION

In accordance with 40 CFR 60.22(b), promulgated on November 17, 1975 (40 FR 53340), this chapter presents a summary of the available information on the potential health and welfare effects of fluorides and the rationale for the Administrator's determination that it is a welfare-related pollutant for purposes of section 111(d) of the Clean Air Act.

The Administrator first considers potential health and welfare effects of a designated pollutant in connection with the establishment of standards of performance for new sources of that pollutant under section 111(b) of the Act. Before such standards may be established, the Administrator must find that the pollutant in question "may contribute significantly to air pollution which causes or contributes to the endangerment of public health or welfare" [see section 111(b)(1)(a)]. Because this finding is, in effect, a prerequisite to the same pollutants being identified as a designated pollutant under section 111(d), all designated pollutants will have been found to have potential adverse effects on public health, public welfare, or both.

As discussed in section 1.1, Subpart B of Part 60 distinguishes between designated pollutants that may cause or contribute to endangerment of public health (referred to as "health-related pollutants") and those for which adverse effects on public health have not been demonstrated ("welfare-related pollutants"). In general, the significance of the distinction is that States have more flexibility in establishing plans for the control of welfare-related pollutants than is provided for plans involving health-related pollutants.

In determining whether a designated pollutant is health-related or welfare-related for purposes of section 111(d), the Administrator considers such factors as: (1) known and suspected effects of the pollutant on public health and welfare; (2) potential ambient concentrations of the pollutant; (3) generation of any secondary pollutants for which the designated pollutant may be a precursor; (4) any synergistic effect with other pollutants; and (5) potential effects from accumulation in the environment (e.g., soil, water and food chains).

It should be noted that the Administrator's determination whether a designated pollutant is health-related or welfare-related for purposes of section 111(d) does not affect the degree of control represented by EPA's emission guidelines. For reasons discussed in the preamble to Subpart B, EPA's emission guidelines [like standards of performance for new sources under section 111(b)] are based on the degree of control achievable with the best adequately demonstrated control systems (considering costs), rather than on direct protection of public health or welfare. This is true whether a particular designated pollutant has been found to be health-related or welfare-related. Thus, the only consequence of that finding is the degree of flexibility that will be available to the States in establishing plans for control of the pollutant, as indicated above.

2.2 EFFECT OF FLUORIDES ON HUMAN HEALTH.[1]

2.2.1 Atmospheric Fluorides

The daily intake of fluoride inhaled from the ambient air is only a few hundredths of a milligram - a very small fraction of the total intake for the average person. If a person is exposed to ambient air containing about 8 micrograms (μg) of fluoride per cubic meter, which is the maximum average concentration that is projected in the vicinity of a fertilizer facility with only mediocre control equipment (Table 9-5), his total daily intake from this source is calculated to be about 150 μg. This is very low compared with the estimated daily intake of about 1200 μg from food, water, and other sources for the average person.

Few instances of health effects in people have been attributed to community airborne fluoride, and they occurred in investigations of the health of persons living in the immediate vicinity of fluoride-emitting industries. The only effects consistently observed are decreased tooth decay and slight mottling of tooth enamel when compared to control community observations. Crippling fluorosis resulting from industrial exposure to fluoride seldom (if ever) occurs today, owing to the establishment of and adherence to threshold limits for exposure of workers to fluoride. It has never been seen in the United States. Even persons occupationally exposed to airborne fluoride do not usually come in contact with fluoride concentrations exceeding the recommended industrial threshold limit values (TLV). The current TLV for hydrogen fluoride is 3 parts per million (ppm) while that for particulate fluoride is 2.5 milligrams per cubic meter (mg/m^3) expressed as elemental fluorine.

There is evidence that airborne fluoride concentrations that produce no plant injury contribute quantities of fluoride that are negligible in terms of possible adverse effects on human health and offer a satisfactory margin of protection for people.

Gaseous hydrogen fluoride is absorbed from the respiratory tract and through the skin. Fluoride retained in the body is found almost entirely in the bones and teeth. Under normal conditions, atmospheric fluoride represents only a very small portion of the body fluoride burden.

2.2.2 Ingested Fluorides

Many careful studies, which were reviewed by the National Academy of Sciences, have been made of human populations living in the vicinity of large stationary sources of fluoride emissions. Even in situations where poisoning of grazing animals was present, no human illness due to fluoride poisoning has been found. In some of these areas much of the food used by the people was locally produced. Selection, processing, and cooking of vegetables, grains and fruits gives a much lower fluoride intake in human diets than in that of animals grazing on contaminated pasture.

In poisoned animals, fluorine levels are several thousand times normal in bone, and barely twice normal in milk or meat. Calves and lambs nursing from poisoned mothers do not have fluorosis. They do not develop poisoning until they begin to graze. Meat, milk and eggs from local animals contain very little more fluoride than the same foods from unpoisoned animals. This is due to the fact that fluorine is deposited in the bones almost entirely.

2.3 EFFECT OF FLUORIDES ON ANIMALS.[1]

In areas where fluoride air pollution is a problem, high-fluoride vegetation is the major source of fluoride intake by livestock. Inhalation contributes only a negligible amount to the total fluoride intake of such animals.

The available evidence indicates that dairy cattle are the domestic animals most sensitive to fluorides, and protection of dairy cattle from adverse effects will protect other classes of livestock.

Ingestion of fluoride from hay and forage causes bone lesions, lameness, and impairment of appetite that can result in decreased weight gain or diminished milk yield. It can also affect developing teeth in young animals, causing more or less severe abnormalities in permanent teeth.

Experiments have indicated that long-term ingestion of 40 ppm or more of fluoride in the ration of dairy cattle will produce a significant incidence of lameness, bone lesions, and dental fluorosis, along with an effect on growth and milk production. Continual ingestion of a ration containing less than 40 ppm will give discernible but nondamaging effects. However, full protection requires that a time limit be placed on the period during which high intakes can be tolerated.

It has been suggested that dairy cattle can tolerate the ingestion of forage that averages 40 ppm of fluoride for a year, 60 ppm for up to 2 months and 80 ppm for up to 1 month. The usual food supplements are low in fluoride and will reduce the fluoride concentration of the total ration to the extent that they are fed.

Fluoride-containing dusts can be non-injurious to vegetation but contain hazardous amounts of fluoride in terms of forage for farm animals. Phosphate rock is an example of a dust that seemingly has not injured plants but is injurious to farm animals. This was made evident forty years ago when an attempt was made to feed phosphate rock as a dietary supplement source of calcium and phosphate. Fluoride injury quickly became apparent.[2] Phosphate rock is used for this purpose today, but only after defluorinating by heat treatment. Phosphate rock typically contains up to about 4 weight percent fluorine.

2.4 EFFECT OF ATMOSPHERIC FLUORIDES ON VEGETATION.[1]

The previous sections state that atmospheric fluorides are not a direct problem to people or animals in the United States, but that animals could be seriously harmed by ingestion of fluoride from forage. Indeed, the more important aspect of fluoride in the ambient air is its effect on vegetation and its accumulation in forage that leads to harmful effects in cattle and other animals. The hazard to these receptors is limited to particular areas: industrial sources having poorly controlled fluoride emissions and farms located in close proximity to facilities emitting fluorides.

Exposure of plants to atmospheric fluorides can result in accumulation, foliar lesions, and alteration in plant development, growth, and yield. According to their response to fluorides, plants may be classed as sensitive, intermediate, and resistant. Sensitive plants include several conifers, several fruits and berries, and some grasses such as sweet corn and sorghum. Resistant plants include several deciduous trees and numerous vegetable and field crops. Most forage crops are tolerant or only moderately susceptible. In addition to differences among species and varieties, the duration of exposure, stage of development and rate of growth, and the environmental conditions and agricultural practices are important factors in determining the susceptibility of plants to fluorides.

The average concentration of fluoride in or on foliage that appears to be important for animals is 40 ppm. The available data suggest that a threshold for significant foliar necrosis on sensitive species, or an accumulation of fluoride in forage of more than 40 ppm would result from exposure to a 30-day average air concentration of gaseous fluoride of about 0.5 micrograms per cubic meter ($\mu g/m^3$).

Examples of plant fluoride exposures that relate to leaf damage and crop reduction are shown in Table 2-1.[2] As shown, all varieties of sorghum and the less resistant varieties of corn and tomatoes are particularly susceptible to damage by fluoride ambient air concentrations projected in the immediate vicinity of fertilizer facilities (See Table 9-5).

2.5 THE EFFECT OF ATMOSPHERIC FLUORIDES ON MATERIALS OF CONSTRUCTION.

2.5.1 Etching of Glass[2]

It is well known that glass and other high-silica materials are etched by exposure to volatile fluorides like HF and SiF_4. Some experiments have been performed where panes of glass were fumigated with HF in chambers. Definite etching resulted from 9 hours exposure at a level of 590 ppb (270 ug/m^3). Pronounced etching resulted from 14.5 hours exposure at 790 ppb (362 ug/m^3). Such levels would, of

Table 2-1. EXAMPLES OF HF CONCENTRATIONS AND EXPOSURE DURATIONS REPORTED TO CAUSE LEAF DAMAGE AND POTENTIAL REDUCTION IN CROP VALUES[2]

Plant	Concentration and Time* Most sensitive varieties - most resistant varieties
Sorghum	0.7 ppb (0.32 $\mu g/m^3$) for 15 days - 15 ppb (6.9 $\mu g/m^3$) for 3 days
Corn	2 ppb (0.92 $\mu g/m^3$) for 10 days - 800 ppb (366 $\mu g/m^3$) for 4 hrs.
Tomato	10 ppb (4.6 $\mu g/m^3$ for 100 days - 700 ppb (321 $\mu g/m^3$) for 6 days
Alfalfa	100 ppb (45.8 $\mu g/m^3$) for 120 days - 700 ppb (321 $\mu g/m^3$) for 10 days

*Concentrations are expressed in terms of parts per billion (ppb) with the equivalent concentration in micrograms per cubic meter ($\mu g/m^3$) given in parenthesis.

course, cause extensive damage to many species of vegatation. However, ambient concentrations of this magnitude are improbable provided that a fertilizer facility properly maintains and operates some type of control equipment for abating fluoride emissions.

2.5.2 Effects of Fluorides on Structures

At the relatively low gaseous concentrations of fluorides in emissions from industrial processes, 1000 ppm or less, the damage caused by fluorides is probably limited mostly to glass and brick. Occasionally, damage to the interior brick lining of a stack has been attributed to fluorides.

Considerable experience is available on corrosion in wet process phosphoric acid plants, where the presence of fluoride increases the corrosive effects of phosphoric acid.[3-5] This experience applies to the liquid phase; the effects of fluoride air emissions need more study. Entrained crude phosphoric acid will corrode structural steel and other non-resistant materials that it settles on, The corrosive effects of "fumes" from the digestion of phosphate rock have been acknowledged and good design and maintenance practices for plant structural steel have been outlined.[6] More information is needed about effects of gaseous fluorides in low concentration outside of the mill. It is usually difficult to separate the corrosive effects of airborne fluorides from those of other local and background pollutants.

2.6 RATIONALE

Based on the information provided the preceding sections of this chapter, it is clear that fluoride emissions from phosphate fertilizer facilities have no significant effect on human health. Fluoride emissions, however, do have adverse effects on livestock and vegetation. Therefore the Administrator has concluded that fluoride emissions from phosphate fertilizer facilities do not contribute to the endangerment of public health. Thus fluoride emissions are considered a welfare-related pollutant for purposes of section 111(d) and Subpart B of Part 60.

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3. PHOSPHATE FERTILIZER INDUSTRY ECONOMIC PROFILE AND STATISTICS

3.1 INDUSTRY STRUCTURE

The phosphate fertilizer industry is a segment of the agricultural chemical industry that is devoted to the production and marketing of commodities bearing the basic nutrients--nitrogen, phosphorous, and potash--for crop production. From the perspective of end-use products, the scope of the agricultural chemical industry includes ammonia, ammonium nitrate, urea, ammonium phosphates, nitrophosphates, mixed plant foods (in varying N-P-K combinations), superphosphates, phosphoric acid, and potash. The phosphate production segment of the agricultural chemical industry begins with the mining of phosphate rock; proceeds with the basic chemical production of phosphoric acid and its subsequent processing to diammonium phosphate (DAP), superphosphoric acid (SPA), and triple superphosphate (TSP); and culminates at the retailer level where the numerous blends of fertilizers are formulated to satisfy the diverse interests of consumers. There are three basic types of retailers - the granular NPK producers (manufacturers of chemical formulations), the liquid fertilizer manufacturers, and the mechanical blenders (dry bulk). These groups compete with each other in some markets (mixed fertilizers).

The basic chemical producers in the industry sell merchant phosphoric acid and products derived from phosphoric acid, such as SPA, DAP, and TSP. NPK producers can therefore buy from a choice of raw materials to produce a specific product. For example, the typical NPK plant operator can buy DAP or produce it from wet-process phosphoric acid. Therefore, some competition can be expected among the various phosphate concentrates.

The basic chemical producers, which are the focus of this analysis, are generally not identifiable as single product firms. Very few firms are totally dependent on fertilizer production for their business. Most fertilizer production is conducted as a subsidiary activity in well diversified, often-times large, corporations. These firms are chemical manufacturers or petrochemical companies. Some companies are farm cooperatives, vertically integrated from production to marketing, in geographic areas in which they are economically based. These latter firms are primarily engaged in serving farm customers by retailing fertilizers, by purchasing and shipping grains and other agricultural products to regional centers, and by providing necessary supplies and services. Finally, there are firms engaged in fertilizer production that derive the main portion of their revenues from totally unrelated activities, such as steel manufacture, pipeline construction, etc.

Generally, the basic chemical producers own the sources of their raw materials (phosphate rock mines). According to 1970 production statistics, the ten largest firms in rock mining are ranked as follows:

TABLE 3-1

TEN LARGEST PHOSPHATE ROCK PRODUCERS[1]

Firm	Production (1000 Short Tons)
International Minerals & Chemicals	8,000
Williams Co. (was Continental Oil Co.)	6,500
Mobil Chemical Company	5,900
Occidental Chemical Company	3,750
American Cyanamid Corp.	3,650
U.S.S. Agrichemicals	3,640

TABLE 3-1 (CONTINUED)

Firm	Production (1000 Short Tons)
Swift & Company	3,000
Texas Gulf, Inc.	3,000
Stauffer Chemical Company	2,500
Gardinier, Inc. (was Cities Service Co.)	2,000
Total	41,940
U.S. Production	50,640
Percent of total production of ten largest firms	83%

Based on the production of wet-process phosphoric acid, the cornerstone of the basic chemical production in the phosphate fertilizer industry, the ten largest firms in terms of 1972 production are as follows:

TABLE 3-2

TEN LARGEST PHOSPHORIC ACID PRODUCERS[2]

Firm	Production Capacity (1000 Short Tons P_2O_5)
CF Industries	880
Freeport Minerals Co.	750
Gardinier , Inc.	544
Farmland Industries	455
Beker Industrial Corp.	411
Texas Gulf Inc.	346
Olin Corporation	337
W.R. Grace & Co.	315
U.S.S. Agri-Chemicals Inc.	266
Occidental Chemical Co.	247
Total	4,551
U.S. Production	6,370
Percent of total production of ten largest firms	71%

A review of the above tabulations reveals vertical integration from the mine through the chemical production within several corporations. Each of the preceding phosphate rock producers owns basic chemical production facilities directly, or through equity interest in chemical producing companies. CF Industries and Farmland Industries are integrated from the chemical production stage forward to the ultimate retailing of fertilizers. Freeport Minerals is strong in ownership of sulfur reserves, an important raw material for production of phosphoric acid. Beker Industries is a newcomer into the fertilizer industry, as they purchased the fertilizer assets of Hooker Chemical (Occidental Petroleum) and El Paso Products Company.

3.2 EXISTING PLANTS

The United States is the world's leading producer and consumer of phosphate fertilizer with an annual consumption of nearly 20 percent of the world's total.[3] Phosphate fertilizers are produced by several processes and consumed in various product forms. Plant statistics are available for those processes of interest under the following classifications: wet-process phosphoric acid, superphosphoric acid, triple superphosphate, and ammonium phosphates.

Tables 3-3 through 3-6 list the company, location, year brought on stream, and annual production capacity of all wet-process phosphoric acid, superphosphoric acid, triple superphosphate, and ammonium phosphate facilities in the United States. Figures 3-1 and 3-2 show the geographic distribution of these plants.

TABLE 3-3
PRODUCTION CAPACITY OF WET-PROCESS PHOSPHORIC ACID (1973) [4,5]

Company	Location	Date on Stream	Annual Capacity (Thousands of Tons P_2O_5)
Allied Chem. Corp.			
Union Texas Petroleum Div. Agricultural Dept.	Geismar, La.	1967	160
Arkansas Louisiana Gas Co.			
Arkla Chem. Corp., subsid.	Helena, Ark.	1967	50
Atlantic Richfield Co.			
ARCO Chem. Co., Div.	Fort Madison, Iowa	1968	225
Beker Indust. Corp.			
Agricultural Products Corp., subsid.	Conda, Idaho	1972	125 (adding 125)
National Phosphate Corp., subsid.	Marseilles, Ill.	1962	105
	Taft, La.	1965	185 (adding 30)
Borden Inc.			
Borden Chem. Div.			
Smith-Douglass	Piney Point, Fla.	1966	165
	Streator, Ill.	1953	25
CF Indust., Inc.			
Bartow Phosphate Complex	Bartow, Fla.	1961	650
Plant City Phosphate Complex	Plant City, Fla.	1965	250 (adding 375)

TABLE 3-3
(CONTINUED)

Company	Location	Date on Stream	Annual Capacity (Thousands of Tons P_2O_5)
Conserv Inc.	Nichols, Fla.	1973	150
Farmland Indust., Inc.	Greenbay, Fla.	1965	500
Freeport Minerals Co. Freeport Chem. Co., Div.	Uncle Sam, La.	1968	750
Gardinier, Inc.	Tampa, Fla.	1961	490
W. R. Grace & Co. Agricultural Chems. Group	Bartow, Fla.	1962	315 (adding 250)
International Minerals and Chemicals Corp.	New Wales, Fla.	1975	(600)
Mississippi Chem. Corp.	Pascagoula, Miss.	1958	130
Mobil Oil Corp. Mobil Chem. Co. Agricultural Chemicals, Div.	Depue, Ill.	1966	130
North Idaho Phosphate Co.	Kellogg, Idaho	1960	30
Occidental Petroleum Corp. Occidental Chem. Co., subsid. Occidental of Florida Div.	White Springs, Fla.	1966	225 (adding 350)
Western Div.	Lathrop, Calif.	1954	17 (adding 23)

TABLE 3-3
(CONTINUED)

Company	Location	Date on Stream	Annual Capacity (Thousands of Tons P_2O_5)
Olin Corp. Agricultural Chems. Div.	Pasadena, Tex.	1965	230 (adding 14)
Pennzoil Co. Pennzoil Chem., Inc., subsid.	Hanford, Calif.	1972	10 (adding 10)
Royster Co.	Mulberry, Fla.	1968	140
J. R. Simplot Co. Minerals and Chem. Div.	Pocatello, Idaho	1962	145 (adding 80)
Stauffer Chem. Co. Fertilizer and Mining Div.	Pasadena, Tex.	1966	60
	Salt Lake City, Utah	1954	65
Texas Gulf, Inc. Agricultural Div.	Aurora, N. C.	1966	350 (adding 350)
Union Oil Co. of California Collier Carbon & Chemical Corp., subsid.	Nichols, Calif.	1961	8
United States Steel Corp. USS Agri-Chemicals, Div.	Bartow, Fla.	1964	95
	Ft. Meade, Fla.	1962	190
Valley Nitrogen Producers, Inc.	Helm, Calif.	1959	35 (adding 83)
	Edison, Calif.	1966	8
The Williams Companies Agrico Chem. Co., subsid.	South Pierce, Fla.	1965	280
	Donaldsonville, La.	1974	(400)
		TOTAL	6,293 (adding 2,690)

TABLE 3-4

PRODUCTION CAPACITY OF SUPERPHOSPHORIC ACID (1973) [4,5]

Company	Location	Date on Stream	Annual Capacity (Thousands of Tons P_2O_5)	Process & Remarks[a]
Allied Chem. Corp. Union Texas Petroleum Div. Agricultural Dept.	Geismar, La.	1967	127	submerged combustion
Beker Indust. Corp. Agricultural Products Corp., subsid.	Conda, Idaho	—	45	vacuum
Farmland Indust., Inc.	Greenbay, Fla.	1971	138	vacuum
Internat'l Minerals & Chem. Corp.	Bartow, Fla.	1963 1967	52 87 139	vacuum: acid is rediluted and used captively to make feed phosphates
North Idaho Phosphate Co.	Kellogg, Idaho	1964	11	vacuum
Occidental Petroleum Corp. Occidental Chem. Co., subsid. Occidental of Florida Div.	White Springs, Fla.	1966	69	submerged combustion
J. R. Simplot Co. Minerals and Chem. Div.	Pocatello, Idaho	1964	32 (adding 23)	vacuum
Stauffer Chem. Co. Fertilizer and Mining Div.	Pasadena, Tex. Salt Lake City, Utah	1966 —	22 34	vacuum vacuum

TABLE 3-4
(CONTINUED)

Company	Location	Date on Stream	Annual Capacity (Thousands of Tons P_2O_5)	Process & Remarks
Texas Gulf, Inc.	Aurora, N. C.	1967	83	vacuum
Agricultural Div.		1970	83	
			166 (adding 82)	
		TOTAL	783 (adding 105)	

[a] Manufactured from wet process phosphoric acid

TABLE 3-5

4-7

PRODUCTION CAPACITY OF TRIPLE SUPERPHOSPHATE (1973)

Company	Location	Date on Stream	Annual Capacity[a] (Thousands of Tons Product)	Product
Beker Indust. Corp. Agricultural Products Corp., subsid.	Conda, Idaho	1974-75	(340)	—
Borden Inc. Borden Chem. Div. Smith-Douglass	Piney Point, Fla.	1966	70	Granular
CF Indust., Inc. Plant City Phosphate Complex	Plant City, Fla.	1965	530 (adding 400)	ROP - granulate portion of production
Conserv Inc.	Nichols, Fla.	1973	280	ROP
Farmland Indust., Inc.	Greenbay, Fla.	1965	190	Granular
Gardinier Inc.	Tampa, Fla.	1952 1972	395 350 745	ROP and granular
W. R. Grace & Co. Agricultural Chems. Group	Bartow, Fla.	1954 1958	390 275 665	ROP and granular
	Joplin, Mo.	1953	100	ROP

TABLE 3-5
(CONTINUED)

Company	Location	Date on Stream	Annual Capacity[a] (Thousands of Tons Product)	Product
Mississippi Chem. Corp.	Pascagoula, Miss.	1972	300	Granular
Occidental Petroleum Corp. Occidental Chem. Co., subsid., Occidental of Florida Div.	White Springs, Fla.	1966	460	Granular
Royster Co.	Mulberry, Fla.	1968	210	ROP
J.R. Simplot Co. Minerals & Chem. Div.	Pocatello, Idaho	1954	120	ROP- granulate portion of production
Stauffer Chem. Co. Fertilizer & Mining Div.	Salt Lake City, Utah	1954	35	ROP- granulate portion of production
Texas Gulf, Inc. Agricultural Div.	Aurora, N.C.	1966	370 (adding 130)	ROP and granular
United States Steel Corp. USS Agri-Chemicals, Div.	Fort Meade, Fla.	1962	295	Granular
The Williams Companies Agrico Chem. Co., subsid.	South Pierce, Fla.	1965	600	ROP- granulate portion of production
		TOTAL	4,970 (adding 870)	

[a] Capacities are for gross weight.

TABLE 3-6

PRODUCTION CAPACITY OF AMMONIUM PHOSPHATES (1973)[4-6]

Company	Location	Date on Stream	Annual Capacity[a] (Thousands of Tons Product)	Remarks
Allied Chem. Corp. Union Texas Petroleum Div. Agricultural Dept.	Geismar, La.	1967	150	DAP, leased to Brewster Phosphates
American Plant Food Corp.	Galena Park, Tex.	1966	175	Mostly mixtures
Arkansas Louisiana Gas Co. Arkla Chem. Corp., subsid.	Helena, Ark.	1967	150	DAP and mixtures
Beker Indust. Corp.				
Agricultural Products Corp., subsid.	Conda, Idaho	1972	270	DAP
National Phosphate Corp., subsid.	Marseilles, Ill.	1962	200	DAP
	Taft, La.	1965	395 (adding 70)	DAP
Borden Inc.				
Borden Chem. Div.	Piney Point, Fla.	1966	130	——
Smith-Douglass	Streator, Ill.	——	90	Mostly mixtures
Brewster Phosphates	Luling, La.	1965	385	DAP
C F Indust., Inc.				
Bartow Phosphate Complex	Bartow, Fla.	1961	1,000	DAP
Plant City Phosphate Complex	Plant City, Fla.	1974	(390)	DAP

TABLE 3-6
(CONTINUED)

Company	Location	Date on Stream	Annual Capacity[a] (Thousands of Tons Product)	Remarks
Conserv Inc.	Nichols, Fla.	1973	200	MAP
Farmland Indust., Inc.	Greenbay, Fla.	1965	390	DAP
	Joplin, Mo.	1954	245	Mixtures
First Mississippi Corp.	Fort Madison, Iowa	1968	495	DAP and Mixtures
Gardinier Inc.	Tampa, Fla.	1959	525	DAP, MAP
W. R. Grace & Co. Agricultural Chems. Group	Bartow, Fla.	1966	235	DAP, MAP
Internat'l Minerals & Chem. Corp.	Bartow, Fla.	1962/63	50	Feed grade DAP and MAP
	New Wales	1975	(490)	DAP and MAP
Kaiser Steel Corp.	Fontana, Calif.	1955	25	Switches between ammonium sulfate and DAP

TABLE 3-6
(CONTINUED)

Company	Location	Date on Stream	Annual Capacity[a] (Thousands of Tons Product)	Remarks
Lone Star Gas Co. Nipak, Inc., subsid.	Kerens, Tex.	1964	110	Mostly mixtures
Mississippi Chem. Corp.	Yazoo City, Miss.	1958	630	Mostly mixtures
Mobil Oil Corp. Mobil Chem. Co. Agricultural Chemicals Div.	Depue, Ill.	1966	240	DAP
Monsanto Co. Monsanto Indust. Chems. Co.	Trenton, Mich.	—	40 - 45	—
North Idaho Phosphate Co.	Kellogg, Idaho	1965	65	DAP, MAP, and mixtures
Occidental Petroleum Corp. Occidental Chem. Co., subsid. Occidental of Florida Div.	White Springs, Fla.	1966	575 (adding 350)	DAP
Western Div.	Lathrop, Calif.	—	165	Mostly mixture
	Plainview, Tex.	—	25	Mostly mixture
Olin Corp. Agricultural Chems. Div.	Pasadena, Tex.	—	800	Mostly mixture
Pennzoil Co. Pennzoil Chem., Inc. subsid.	Hanford, Calif.	1973	—	MAP
Royster Co.	Mulberry, Fla.	1968	270	DAP
J. R. Simplot Co. Minerals and Chem. Div.	Pocatello, Idaho	1961	190 (adding 50)	DAP and MAP

TABLE 3-6
(CONTINUED)

Company	Location	Date on Stream	Annual Capacity[a] (Thousands of Tons Product)	Remarks
Standard Oil Company of Calif. Chevron Chem. Co., subsid.	Fort Madison, Iowa	1962	200	Mixtures
	Kennewick, Wash.	1959	75	Mixtures
	Richmond, Calif.	1957	100	Mixtures
Stauffer Chem Co. Fertilizer & Mining Div.	Pasadena, Tex.	1966	135	Mostly DAP &
	Salt Lake City, Utah	1965	65	Mostly DAP &
Tennessee Valley Authority	Muscle Shoals, Ala.	1966	33	Solid ammoniu polyphosphate
Texas Gulf, Inc. Agricultural Div.	Aurora, N. C.	1966	220	DAP
Union Oil Co. of California Collier Carbon and Chem. Corp. subsid.	Nichols, Calif.	1957	55	Mostly mixtur
United States Steel Corp. USS Agri-Chemicals, Div.	Cherokee, Ala.	1962	245	DAP & mixture
Valley Nitrogen Producers, Inc.	Bakersfield, Calif.	1960	10	8 - 24 - 0
	Helm, Calif.	1959	140 (adding 150)	MAP & mixture
Arizona Agrichemical Corp., subsid.	Chandler, Arizona	1967	60	Map, 16 - 20
The Williams Companies Agrico Chemical Co., subsid.	Donaldsonville, La.	1969	700 (adding 840)	DAP
		TOTAL	10,288 (adding 2,340)	

[a] Capacities are for gross weight of product and includes diammonium phosphate (DAP), monammonium phosphate (MAP ammonium phosphate sulfate and ammonium phosphate nitrate.

FIGURE 3-1

TRIPLE SUPERPHOSPHATE AND AMMONIUM PHOSPHATE PLANT LOCATIONS

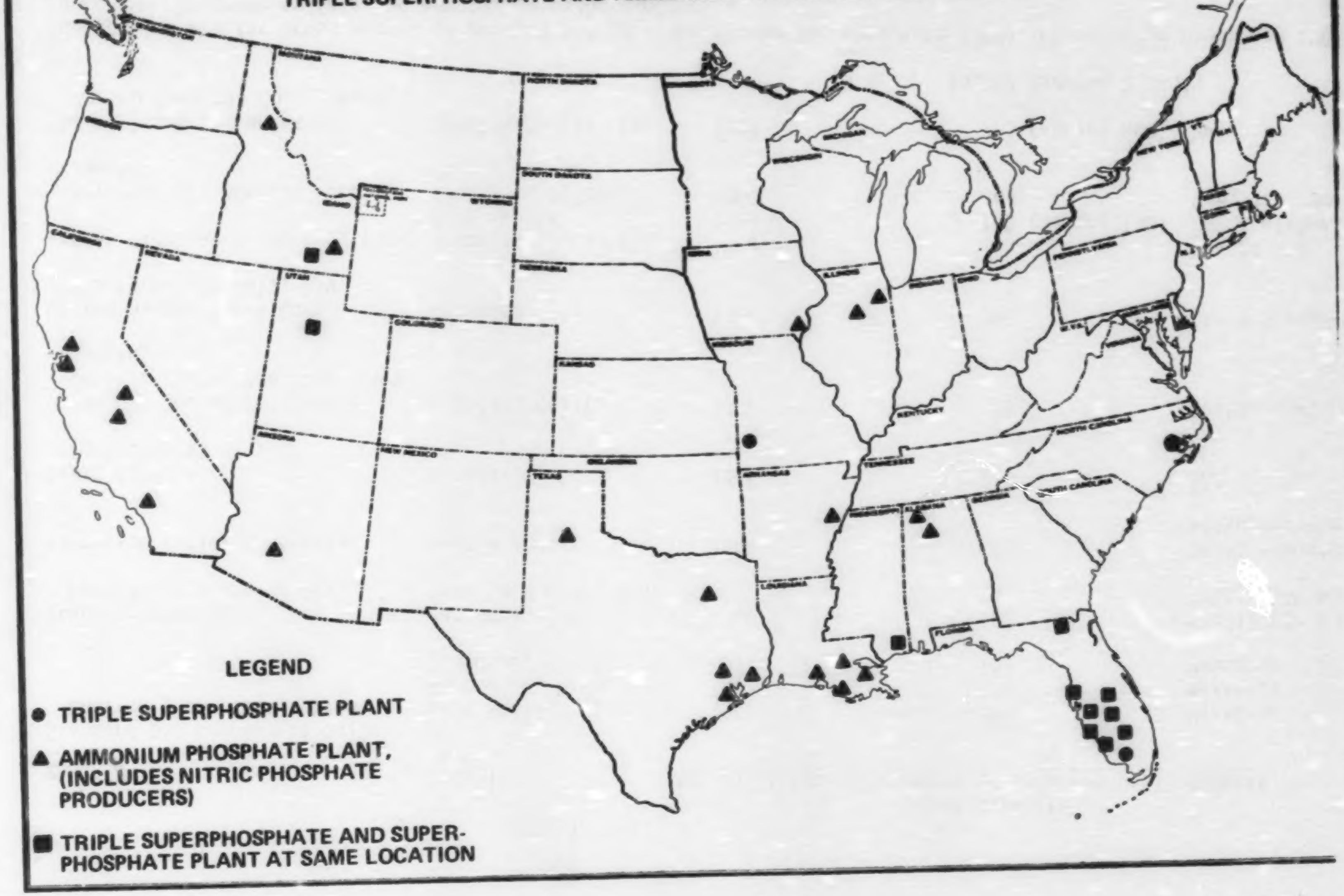
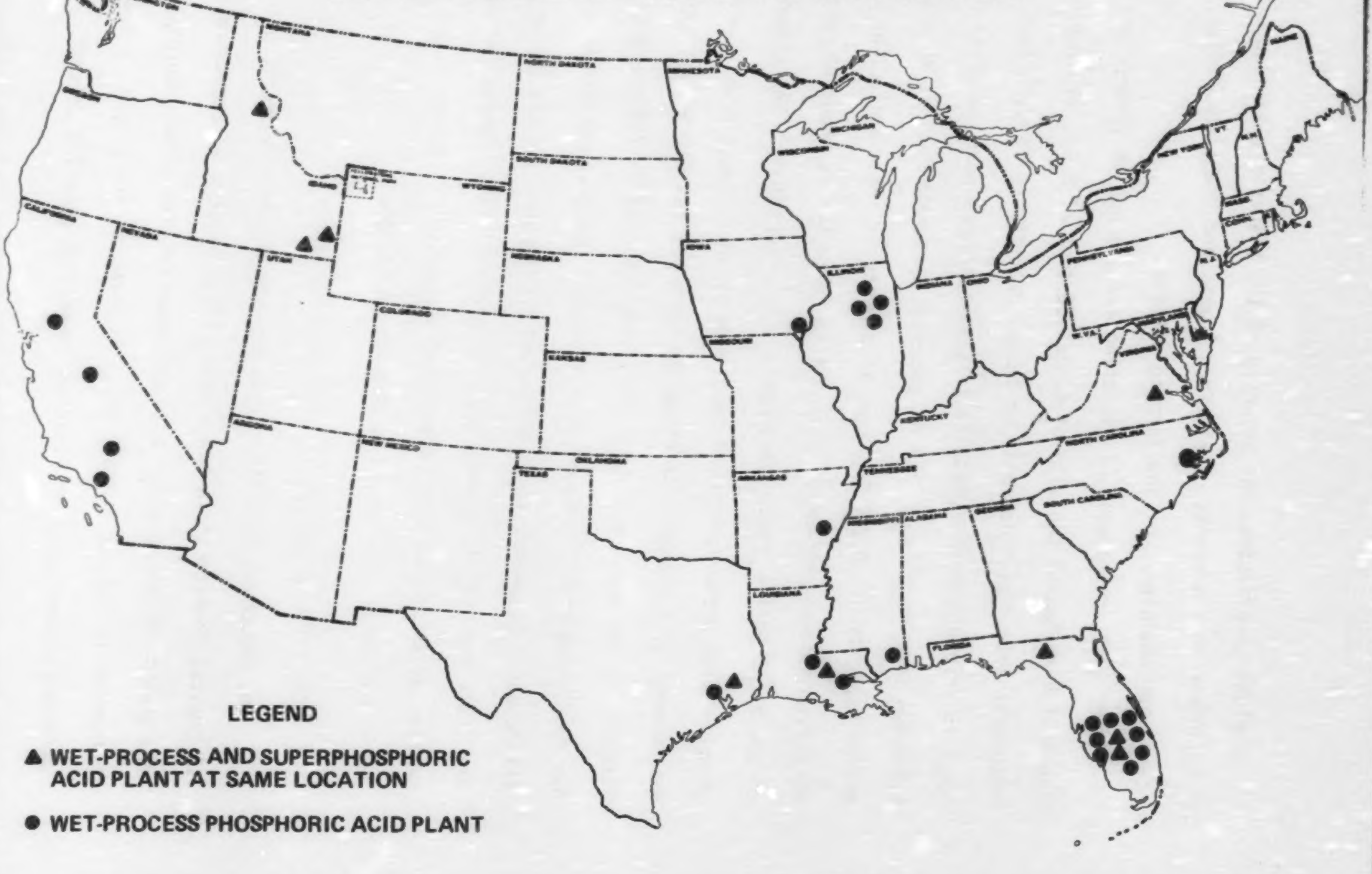

NORTH DAKOTA
SOUTH DAKOTA
UTAH
COLORADO
KANSAS
NEW MEXICO
TEXAS
KENTUCKY
NORTH CAROLINA
SOUTH CAROLINA
FLORIDA
VT.
LEGEND
● TRIPLE SUPERPHOSPHATE PLANT
▲ AMMONIUM PHOSPHATE PLANT, (INCLUDES NITRIC PHOSPHATE PRODUCERS)
■ TRIPLE SUPERPHOSPHATE AND SUPER-PHOSPHATE PLANT AT SAME LOCATION

FIGURE 3-2

WET-PROCESS AND SUPERPHOSPHORIC ACID PLANT LOCATIONS


LEGEND
▲ WET-PROCESS AND SUPERPHOSPHORIC ACID PLANT AT SAME LOCATION
● WET-PROCESS PHOSPHORIC ACID PLANT

As might be expected, the majority of the plants are located either near the phosphate rock deposits of Florida, Idaho, and Utah; the sulfur deposits of Texas and Louisiana; or the farming outlets.

As of 1973, there were 34 operating wet-process phosphoric acid plants with an annual capacity of 6,435,000 tons of P_2O_5; 10 superphosphoric acid facilities with an annual capacity of 783,000 tons of P_2O_5; 15 triple superphosphate facilities with an annual capacity of 4,970,000 tons of product, and 44 ammonium phosphate facilities with an annual capacity of 10,280,000 tons of product.[4-6] The production capacity attributed to wet-process acid plants in Table 3-3 is about 80 percent of the total United States phosphoric acid production. The balance is produced from elemental phosphorous made by the furnace method, which is not covered by the standards of performance for new stationary sources (SPNSS) for the phosphate fertilizer industry. Table 3-5 presents statistics for facilities producing both run-of-pile triple superphosphate and granular triple superphosphate; it is estimated that between 60 and 70 percent of the total capacity is associated with granular TSP. Approximately 70 percent of the production capacity of ammonium phosphates listed in Table 3-6 can be attributed to diammonium phosphate.

3.3 CAPACITY UTILIZATION

The phosphate fertilizer industry has followed a cyclic pattern of capital investment in new plants. This pattern is demonstrated by the graphs for phosphoric acid and ammonium phosphate production presented in Figures 3-3 and 3-4. As shown in the graphs by the duration between peak utilization (operating near 100 percent), the cycle length appears to be 6 to 7 years. During the 1965 to 1972 cycle, expansion peaked in 1969. Slackened demands prompted price cutting and eventual temporary shutdown of some facilities. At the end of the cycle, supply of plant capacity came in balance with production.

For additional insight into the cyclic trend of capacity utilization, Table 3-7 lists operating ratios for phosphoric acid and diammonium phosphate production.

TABLE 3-7
PRODUCTION AS PERCENT OF CAPACITY[8]

Year	WPPA	DAP
1965	100	72
1966	92	63
1967	80	66
1968	77	56
1969	69	54
1970	84	78
1971	96	96
1972	96	96
1973	89	--
1974	89	--
1975	83	--
1976	82	--

During mid-1973, the industry was operating near capacity. Idle plants that had been shutdown during the 1968-1970 recession were being refurbished for production. Beker Industries is one example of a firm that purchased idle phosphate facilities from petroleum companies for acid and ammonium production. New plant construction, as announced by Agrico Chemical and IMC, will not provide significant additions to supply of phosphates until 1975 or 1976. By inspection of the profiles in Figures 3-3 and 3-4 and the operating ratios presented in Table 3-7, planned plant capacity for phosphoric acid seems sufficient through 1976; ammonium phosphate capacity, on the other hand, will have to be increased to cope with the projected demand.

3.4 CONSUMPTION PATTERNS

For an understanding of the historical consumption patterns of WPPA, SPA, DAP, and TSP, an overview of consumption of all phosphate fertilizers is presented. Although some superphosphoric acid is consumed in the form of animal feed supplements, most phosphate production from wet-process phosphoric acid ends up in fertilizers.

Historical data are presented for U.S. consumption in Table 3-8. Liquids and solids (bulk and bagged) are all included in these data. Total consumption includes phosphate values derived from wet-process phosphoric acid to produce triple superphosphate, and phosphate rock reacted with sulfuric acid to produce normal superphosphate.

Overall, the growth trend in total consumption has been at a rate of 6.5 percent compounded annually from the base year 1960. However, normal superphosphate production has declined steadily from 1,270,000 tons (P_2O_5) in 1960 to 621,000 tons (P_2O_5) in 1973.[9] The gap in phosphate values generated by the decline in NSP has been mostly taken up by diammonium phosphate production, as well as wet-process phosphoric acid, the intermediate product. Hence, consumption of wet-process phosphoric acid and diammonium phosphate production have grown at a more rapid rate than total consumption of phosphates.

FIGURE 3-3. CAPACITY UTILIZATION OF WET-PROCESS PHOSPHORIC ACID[10,11]

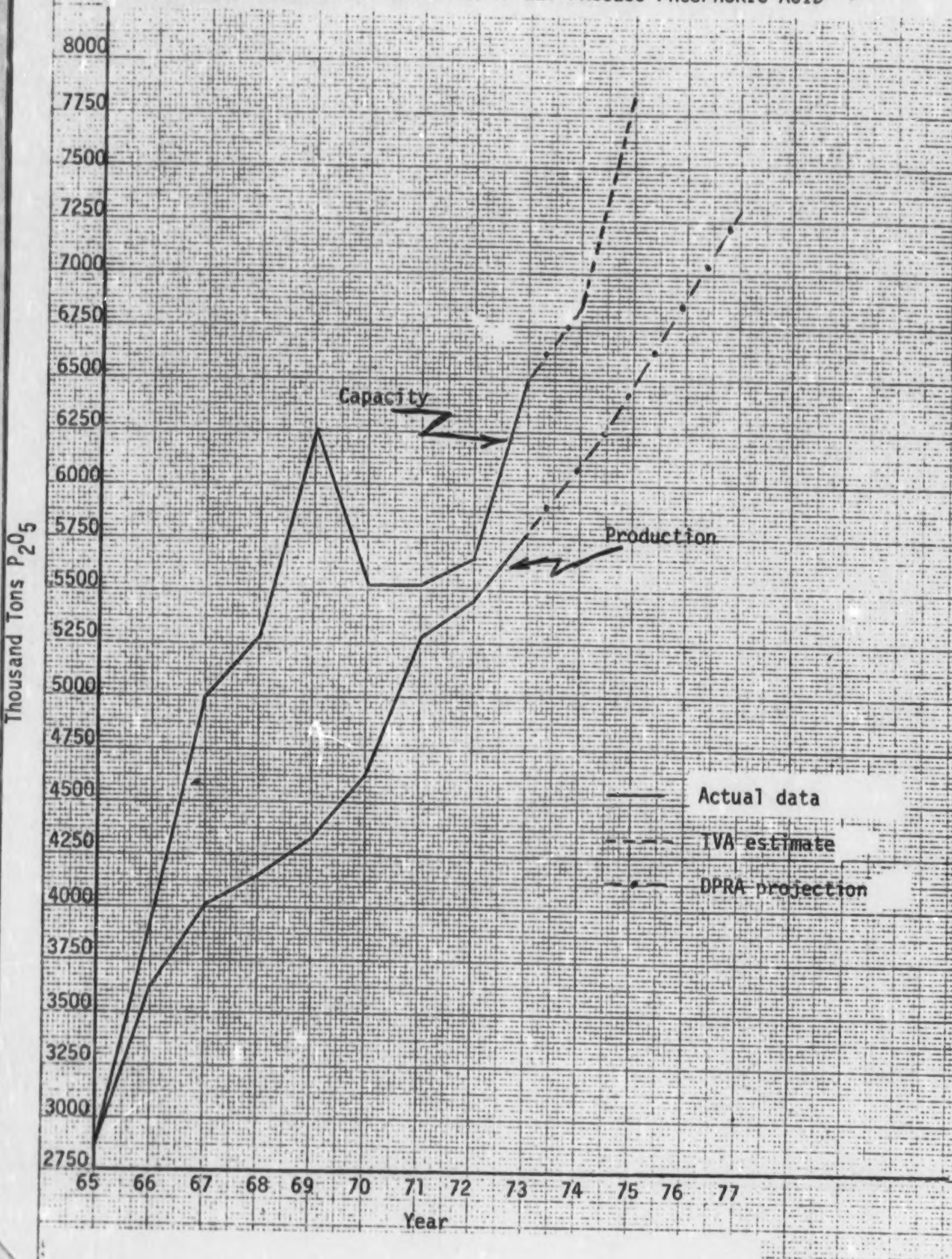
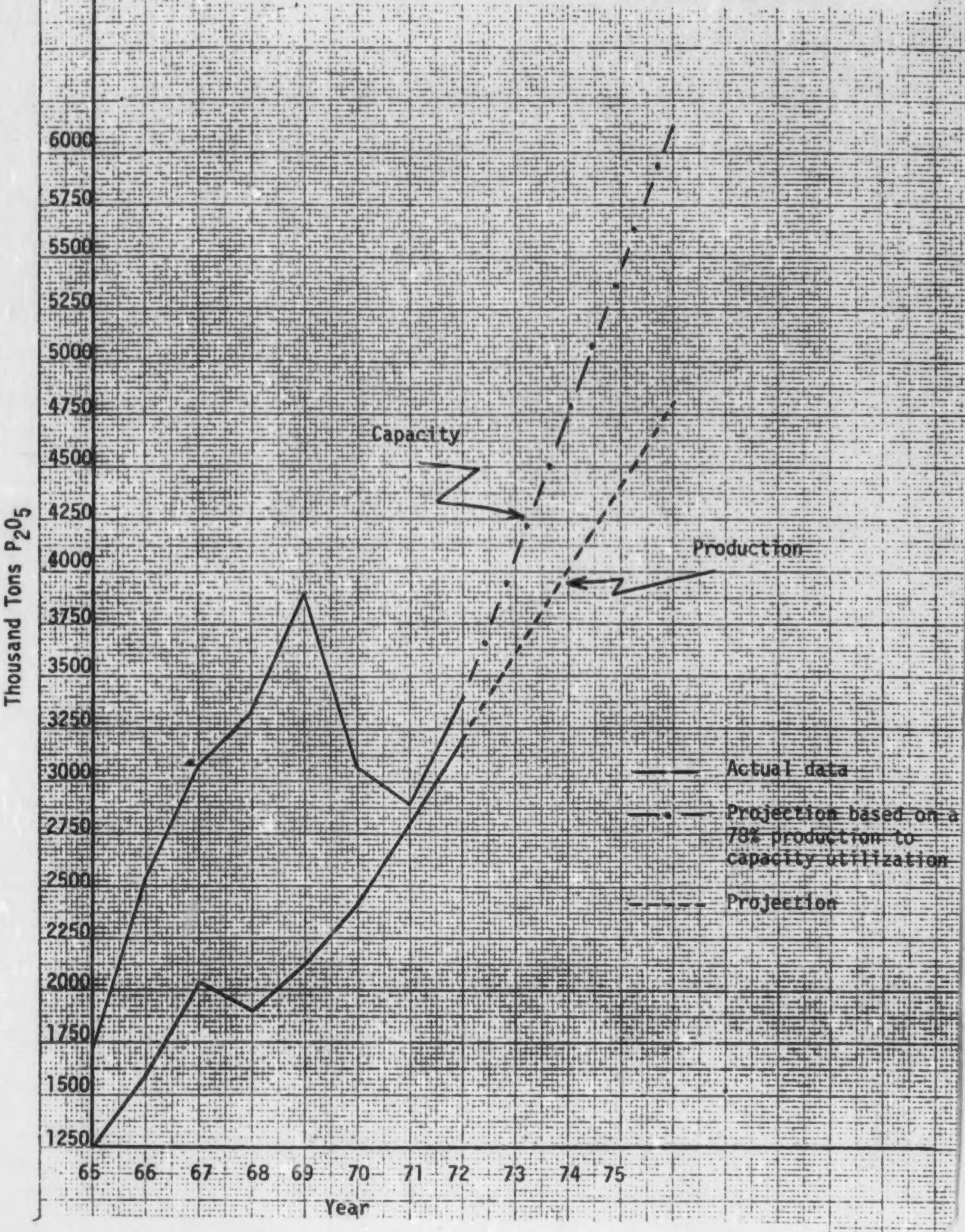


FIGURE 3-4. CAPACITY UTILIZATION OF AMMONIUM PHOSPHATES[12]



The two other major categories presented in Table 3-8 separate the basic chemicals that are applied directly to the soil from those that receive further processing into mixtures; foods containing at least two of the nutrients basic to plant growth. Some duplication of reporting is evident in the statistics as some undetermined amount appears twice, in "mixtures" and "direct applications".

Review of the data in Table 3-8 shows that the demand for normal superphosphate has decreased drastically in recent years. During this same time period, the use of ammonium phosphates (other than DAP) and triple superphosphate have slowed while the demand for DAP has grown steadily. Almost all direct application materials are now DAP or GTSP. Demand for these materials appears to have grown more rapidly than total consumption. Additional factors contributing to this trend are the rise of bulk blending operations and intensive cultivation (emphasis on increased yield per acre).

Farmers have lately realized that mechanical blends of grandulated concentrates do just as well as a grandulated, chemically produced NPK food and are available at lower costs. A shift from normal superphosphate and run-of-pile triple superphosphate production to the grandulated concentrates, DAP, and GTSP, is occurring.

The shift in product usage has also been accompanied by a shift in raw materials for NPK plants. Run-of-pile triple superphosphate has been replaced by wet-process phosphoric acid as a raw material. Improvement in phosphoric acid technology has made it possible to inhibit the precipitation of imputities during shipping, as most NPK plants are far removed from the areas of acid production.

TABLE 3-8. U.S. PHOSPHATE CONSUMPTION, 1960-1973
(1000 tons P_2O_5)[13]

Year	Total Consumption	Mixtures	Direct Application Materials			
			Diammonium Phosphates[a]	Normal Superphosphate	Triple Superphosphate	Ammonium Phosphates[b]
1960	2572	2033	35	103	185	171
1961	2645	2069	63	100	203	188
1962	2807	2219	110	97	217	205
1963	3073	2474	177	98	220	205
1964	3378	2705	244	93	289	216
1965	3512	2816	302	95	309	204
1966	3897	3111	418	94	413	221
1967	4305	3503	451	86	432	224
1968	4452	3579	608	79	487	227
1969	4666	3724	724	72	585	207
1970	4574	3709	726	62	546	184
1971	4803	3943	814	55	556	179
1972	4873	4007	884	44	577	174
1973[c]	5072	4200	-	35	569	-

[a] Includes grades 18-46-0 and 16-48-0

[b] Includes grades 11-48-0, 13-39-0, 16-20-0, 21-53-0, and 27-14-0

Consumption of superphosphoric acid is only recently beginning to expand. To date, it has been used primarily for the production of liquid fertilizers with some secondary end-use in the production of animal feed supplements. Data for consumption is limited. Superphosphoric acid consumption is currently estimated at only 15 percent of overall phosphate consumption.

Several reasons are presented to explain the expected expansion of superphosphoric acid consumption. Technology has made it possible to produce a product which eliminates the problems of sludge formation encountered during shipping and storage of wet-process acid. Increased crop yield per unit P_2O_5 applied from liquid fertilizers has been claimed. Transportation costs per ton of P_2O_5 are less for liquid than for solid fertilizers.

The implications of the shifting patterns in the industry in response to demands for cheaper, better quality products are as follows:

1. Granular concentrates will continue to expand in production; these include DAP and GTSP.
2. Run-of-pile TSP production will decline and be replaced by GTSP and DAP.
3. Superphosphoric acid will have the largest growth rate of all phosphate commodities.

3.5 FUTURE TRENDS

The phosphate fertilizer industry has experienced dynamic growth in recent years. Table 3-9 provides production statistics for wet process phosphoric acid, triple superphosphate, and ammonium phosphates

TABLE 3-9

U.S. PRODUCTION OF THREE COMMODITIES IN THE PHOSPHATE INDUSTRY, 1950-1973[14]

Year	Wet Process Phosphoric Acid	Triple Superphosphate	Ammonia[a] Phosphates
	(Thousand tons of P_2O_5)		
1950	299	309	-
1955	775	707	-
1960	1,325	986	269
1961	1,409	1,024	370
1962	1,577	960	536
1963	1,957	1,113	-
1964	2,275	1,225	-
1965	2,896	1,466	1,081
1966	3,596	1,696	1,376
1967	3,993	1,481	1,747
1968	4,152	1,387	1,633
1969	4,328	1,354	1,844
1970	4,642	1,474	2,092
1971	5,016	1,503	2,395
1972	5,594[b]	1,659	2,577
1973	5,621[b]	1,716[b]	2,665[b]

---

[a] Includes diammonium phosphate, monammonium phosphate, ammonium phosphate sulfate, ammonium phosphate nitrate, and other phosphate fertilizers.

[b] Preliminary.

from 1950 to 1973. During this period, wet-process phosphoric acid has shown a strong steady growth because of its role as an intermediate in the production of ammonium phosphates, triple superphosphate, and other phosphate products. Production of wet acid has grown at an average annual rate of 14 percent since 1960. Table 3-3 lists announced construction of wet acid plants through 1975. This new construction will increase total capacity by 41.6 percent. An average annual growth rate of 6.0 percent is expected for the period from 1976 to 1980.[15]

Documentation of superphosphoric acid production is very limited. The usual reporting groups, such as Department of Commerce and TVA, do not report production figures. The Fertilizer Institute reports production in its Fertilizer Index but privately concedes that its published figures for the years of 1969-1971 are below estimates of actual production.

A 40 percent saving in freight costs per unit weight of P_2O_5 is realized when phosphoric acid is shipped in the concentrated superacid form.[16] Anticipated growth for superphosphoric acid is largely due to this reduced shipping cost and the availability of merchant grade wet-process acid will be a major factor affecting expansion. Announced construction through 1975 will increase existing capacity by approximately 13 percent. Rapid growth during the remainder of the decade is expected.

By definition, ammonium phosphates are products manufactured directly from ammonia, phosphoric acid, and sometimes other acids, in contrast to those ammoniated phosphates that are produced in NPK granulation plants from ammonia and run-of-pile triple superphosphate. "Diammonium" phosphates include 16-48-0 (N, P_2O_5, and K_2O content) and 18-46-0 grades. Monammonium phosphates are 11-48-0. These two generic products are produced strictly from ammonia and phosphoric acid; other ammonium phosphates are produced from a mixture of ammonia, phosphoric acid, nitric acid, and possibly sulfuric acid.

The growth of ammonium phosphates has been more rapid than that of triple superphosphates - 20 percent annual growth since 1960 - because of several inherent advantages of ammonium phosphates (see Section 4.4). New construction through 1975 will increase production capacity by 22.7 percent. Annual growth from 1975 to 1980 is projected at 6 percent.[15]

Production of triple superphosphate has grown at an average annual rate of 4 percent since 1960. Triple superphosphate is produced by two methods; the den method and the granulator method. The den method produces a material (run-of-pile) that is non-uniform in particle size. This material is stored, pulverized, and shipped to NPK plants for ammoniation. The granulator method produces a granular product that is sold to bulk blender retailers for mixing or for direct application (as a 0-46-0 fertilizer) to the soil.

No statistics are available as to the breakdown of run-of-pile versus direct granulator production. In the industry, run-of-pile production by the primary producer may be granulated and sold as GTSP to bulk blender retailers as a direct application fertilizer. Ultimately, essentially all run-of-pile production becomes granulated, either by the primary producer or by the NPK plant. Only granulated TSP is expected to be of importance in the future.

Announced new construction through 1975 will result in a 17.4 percent increase in triple superphosphate production capacity, however, this apparent growth does not take into consideration the possible closings of existing run-of-pile facilities. Granular triple superphosphate production should experience an average annual growth of 4 percent from 1975 to 1980.[15]

There appears to be a trend toward larger production facilities in the phosphate fertilizer industry. Average plant life is from 10 to 15 years and older plants are generally replaced by larger ones employing the latest proven technology. A number of small experimental plants have been built that produce such products as ultraphosphoric acid (83 percent P_2O_5), ammonium polyphosphate (15-61-0, NPK content) and high analysis superphosphate (54 percent P_2O_5) but this experimental technology has not yet been applied to large scale production. All indications are that the phosphate fertilizer industry will continue to grow rapidly throughout the 1970-1980 decade.

3.6 PRICES

Price competition in the fertilizer industry has been very intense historically because of the large number of participants in all facets of manufacturing--basic chemical producers, manufacturers of mixed fertilizers, blenders, and retailers. No one chemical producer can be said to be a price leader. The participation of farm cooperatives in the manufacturing segment of fertilizers, including the basic chemicals, undoubtedly has been a steadying factor on prices, minimizing cyclic fluctuations.

List prices are available for (agricultural grade) wet-process phosphoric acid, triple superphosphate (run-of-pile and granular), diammonium phosphate, and superphosphoric acid in the Chemical Marketing Reporter published by Snell Publishing Company of New York. These prices are not firm indicators of actual prices paid, however, since discounts, variability in credit terms to buyers, and service fees combine to determine the realized price available to the producer.

The long term profiles of wholesale prices for granular triple superphosphate and diammonium phosphate are presented in Figure 3-5. The estimates of prices realized by manufacturers are plotted against the ranges of listed quotations for the same products for 1971 and 1972. The spreads in prices reflect the difference in quotations by various manufacturers at any given time. No long term profiles of prices are available for wet-process phosphoric acid, superphosphoric acid, and triple superphosphate.

July 1974 phosphate fertilizer list prices are presented in Table 3-10. The prices presented later in the text (Table 7-1) reflect estimated averages for November 1974 developed from a more recent economic study. These averages reflect more closely prices realized by the producers and will be used in measuring the economic assessment of emission guidelines in Section 7.

FIGURE 3-5. WHOLESALE PRICES FOR TRIPLE SUPERPHOSPHATE AND DIAMMONIUM PHOSPHATE

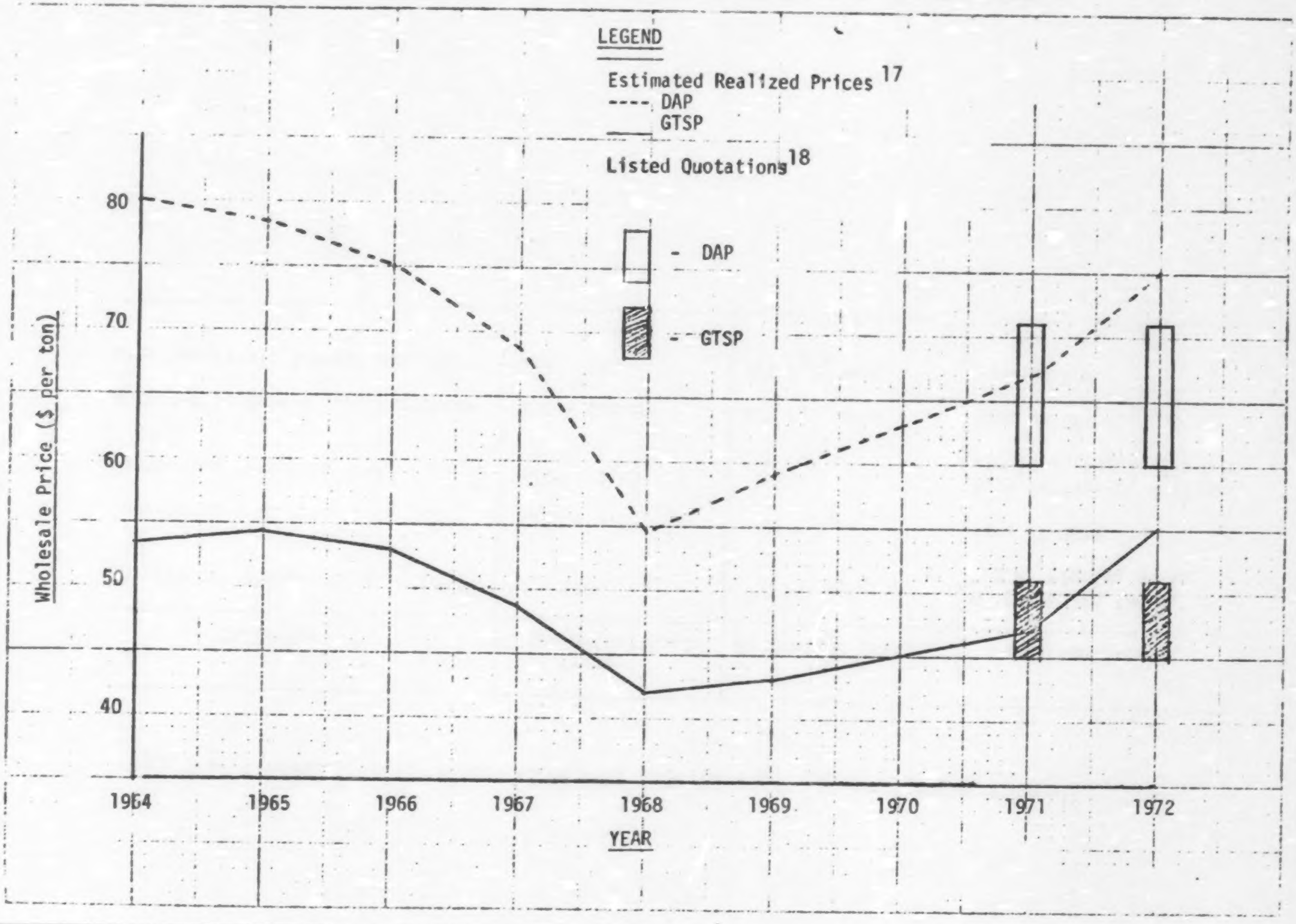


TABLE 3-10. SUMMARY OF LIST PRICES AS OF JULY 1974 AND BASIS FOR PHOSPHATE QUOTATION[19]

Commodity	Price ($ per actual ton)	Production Quality	Quotation Basis
Wet-process phosphoric acid (WPPA)	$105	52-54% P_2O_5	Delivered in Tanks, F.O.B. Florida works
Superphosphoric acid (SPA)	$150 - $158	70% P_2O_5	Same as WPPA
Diammonium Phosphate (DAP)	$145 - $165	18%N 46% P_2O_5	Bulk Delivered, Railroad car lots, F.O.B. Florida
Run-of-Pile Triple Superphosphate	$38 - $86.50	46% P_2O_5 min	Same as DAP
Granular Triple Superphosphate	$55 - $91	46% P_2O_5 min	Same as DAP

3.7 WORLD STATISTICS ON P_2O_5

The levels of crop yields per acre have greatly increased during the past generation. This increase has depended upon the generous application of fertilizers containing the elements phosphorus, nitrogen, and potassium. No two of these elements together could maintain high crop levels; therefore, plentiful application of P_2O_5 will continue to be necessary even to maintain food production at its current level.

Table 3-11 shows U.S. consumption of phosphate fertilizer expressed as P_2O_5 and the corresponding consumption for the entire world is given for comparison. The data from the reference are adapted to this table and are rounded off.

Phosphate fertilizer is made almost entirely from phosphate rock and this is the only practical source for the quantities required. Table 3-12 shows the total known world reserves of phosphate rock. The United States has 30 percent of the supplies which are considered mineable and beneficiable by current technology. The Arab Nations possess 50 percent of world reserves and the Soviet Union has an additional 16 percent. It must not be inferred that reserves within a country are uniform in quality; the higher grades are mined first, and successfully poorer grades follow at increased energy consumption and cost rates.

TABLE 3-11
UNITED STATES AND WORLD CONSUMPTION OF PHOSPHATE FERTILIZER[3]

Fiscal Year	Consumption of Phosphate Fertilizer Million Short Tons P_2O_5	
	U.S.	World
1950	1.950	6.45
1955	2.284	8.33
1960	2.572	10.52
1965	3.512	15.03
1970	4.574	20.40
1975	5.800*	

*Estimated

TABLE 3-12
WORLD RESERVES OF PHOSPHATE ROCK[20]

Country	Million Short Tons P_2O_5
French Morocco	23,500
U.S.	16,250
U.S.S.R.	8,500
Tunisia	2,240
Algeria	1,120
Brazil	670
Peru	500
Egypt	220
Togo	130
Spanish Sahara	110
Islands - Pacific & Indian Ocean	45
Senegal	45
Other Countries	800

3.8 REFERENCES

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15. Bunyard, F.L. and P.A. Boys. The Impact of New Source Performance Standards upon the Phosphate Fertilizer Industry. Environmental Protection Agency. Durham, North Carolina. August 25, 1973.

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4. PHOSPHATE FERTILIZER PROCESSES

4.1 INTRODUCTION.

The phosphate fertilizer industry uses phosphate rock as its major raw material. After preparation, the rock is used directly in the production of phosphoric acid, normal superphosphate, triple superphosphate, nitrophosphate, electric furnace phosphorous and defluorinated animal feed supplements. In addition to those products made directly from phosphate rock, there are others that rely on products produced from phosphate rock as a principal ingredient. Figure 4-1 illustrates the major processing steps used to transform phosphate rock into fertilizer products and industrial chemicals.

The primary objective of the various phosphate fertilizer processes is to convert the fluorapatite ($Ca_{10}(PO_4)_6F_2$) in phosphate rock to soluble P_2O_5, a form readily available to plants. Fluorapatite is quite insoluble in water and, in most farming situations, is of little value as a supplier of nutrient phosphate. The most common method of making the P_2O_5 content of phosphate rock available to plants is by treatment with a mineral acid - sulfuric, phosphoric, or nitric. Table 4-1 lists the available P_2O_5 content of several phosphate fertilizers. Available P_2O_5 is defined as the percent soluble P_2O_5 in a neutral citrate solution.

FIGURE 4-1. MAJOR PHOSPHATE ROCK PROCESSING STEPS [1]

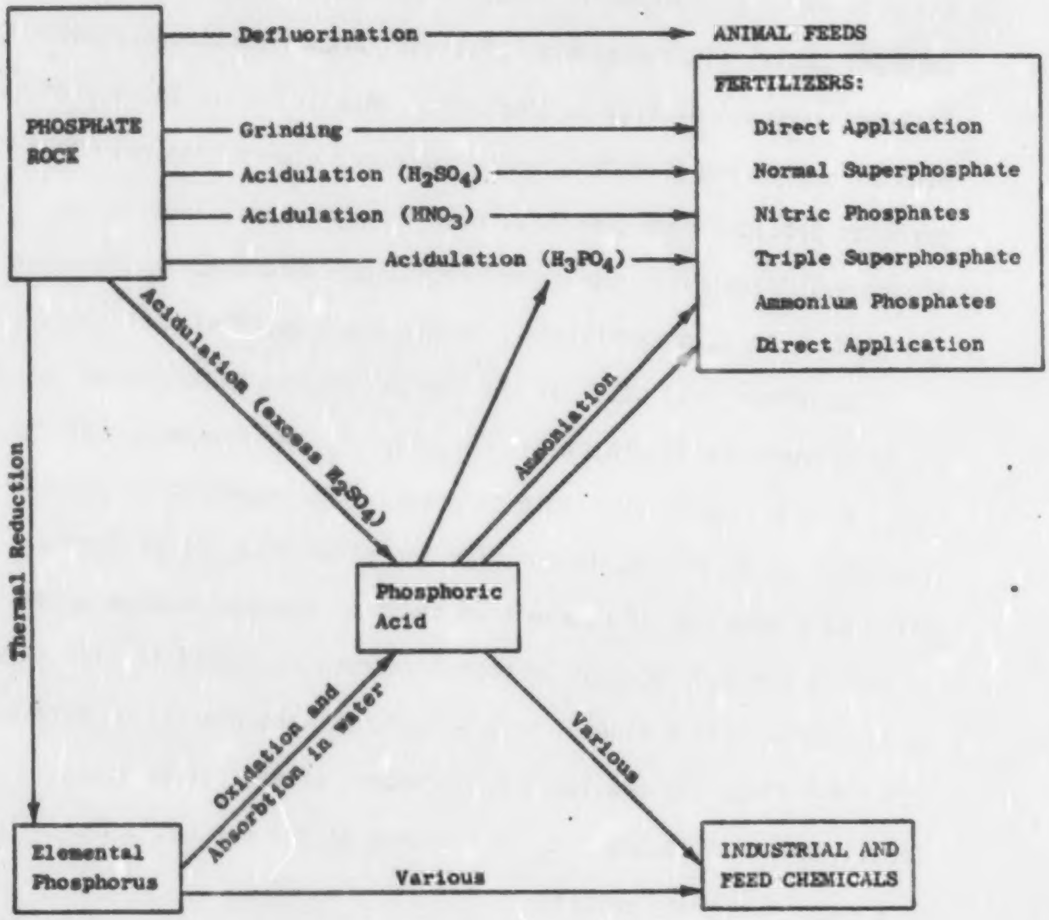

PHOSPHATE ROCK
Defluorination
ANIMAL FEEDS
Grinding
Acidulation (H_2SO_4)
Acidulation (HNO_3)
Acidulation (H_3PO_4)
FERTILIZERS:
Direct Application
Normal Superphosphate
Nitric Phosphates
Triple Superphosphate
Ammonium Phosphates
Direct Application
Acidulation (excess H_2SO_4)
Ammoniation
Thermal Reduction
Phosphoric Acid
Oxidation and Absorbtion in water
Various
Elemental Phosphorus
Various
INDUSTRIAL AND FEED CHEMICALS

TABLE 4-1. P_2O_5 CONTENT OF PHOSPHATE FERTILIZERS[2]

FERTILIZER	PERCENT SOLUBLE P_2O_5
Normal Superphosphate	16 - 22
Triple Superphosphate	44 - 47
Monammonium Phosphate	52
Diammonium Phosphate	46

4.2 WET PROCESS PHOSPHORIC ACID MANUFACTURE.

Phosphoric acid is an intermediate product in the manufacture of phosphate fertilizers. It is subsequently consumed in the production of triple superphosphate, ammonium phosphates, complex fertilizers, superphosphoric acid and dicalcium phosphate.

Most current process variations for the production of wet-process phosphoric acid depend on decomposition of phosphate rock by sulfuric acid under conditions where gypsum ($CaSO_4 \cdot 2H_2O$) is precipitated. These variations are collectively referred to as dihydrate processes since the calcium sulfate is precipitated as the dihydrate (gypsum). Calcium sulfate can also be precipitated in the semihydrate ($Ca\ SO_4 \cdot 1/2\ H_2O$) and anhydrite ($CaSO_4$) forms. Processes which accomplish this are commercially less important than the dihydrate processes, however, since they require more severe operating conditions, higher temperatures, and a greater degree of control.

The overall reaction in the dihydrate processes is described by the following equation. (4-1)

$$3\ CA_{10}\ (PO_4)_6\ F_2 + 30H_2SO_4 + SiO_2 + 58H_2O \rightarrow 30CaSO_4 \cdot 2\ H_2O + 18H_3PO_4 + H_2SiF_6$$

In practice, 93 or 98 percent sulfuric acid is normally used for digestion of the rock. Calcium sulfate precipitates, and the liquid phosphoric acid is separated by filtration.

Several variations of the dihydrate process are currently in use by the phosphate fertilizer industry. The Dorr-Oliver, St. Gobain, Prayon, and Chemico processes are among the better known designs. Fundamentally, there is little difference among these variations - most differences are in reactor design and operating parameters. Figure 4-2 presents a flow diagram of a modern wet-process phosphoric acid plant.

Finely-ground phosphate rock is continuously metered into the reactor and sulfuric acid is added. Because the proper ratio of acid to rock must be maintained as closely as possible, these two feed streams are equipped with automatic controls.

Some years ago, plants were built with several separate reaction tanks connected by launders, which are channels for slurry flow. The tendency now is to use a single tank reactor that has been divided into several compartments. In most of these designs, a series of baffles is used to promote mixing of the reactants.

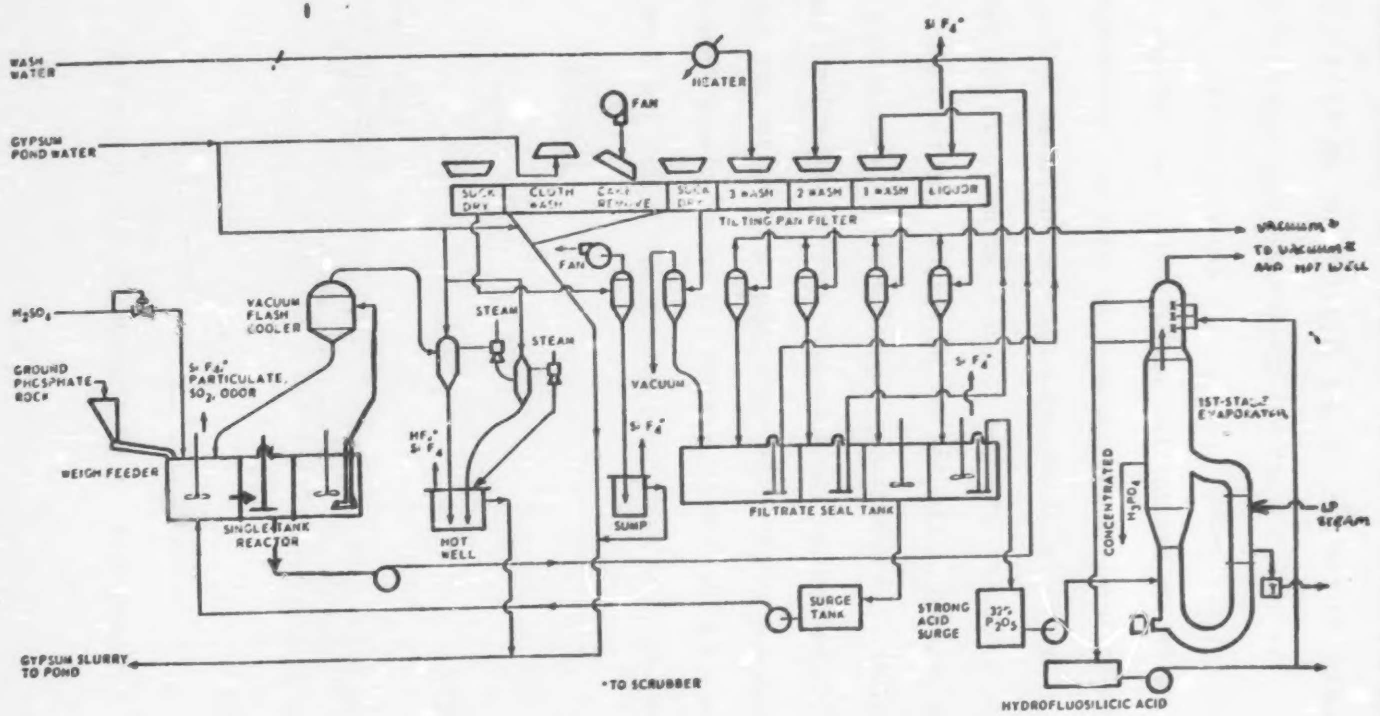

WASH WATER
GYPSUM POND WATER
H_2SO_4
GROUND PHOSPHATE ROCK
WEIGH FEEDER
SiF_4*, PARTICULATE, SO_2, ODOR
SINGLE-TANK REACTOR
VACUUM FLASH COOLER
STEAM
STEAM
HF_4* SiF_4
HOT WELL
FAN
FAN
HEATER
SUCK DRY
CLOTH WASH
CAKE REMOVE
SUCK DRY
3 WASH
2 WASH
1 WASH
LIQUOR
TILTING PAN FILTER
SiF_4*
VACUUM
SiF_4*
SUMP
SiF_4*
FILTRATE SEAL TANK
SURGE TANK
STRONG ACID SURGE
32% P_2O_5
VACUUM*
TO VACUUM* AND HOT WELL
1ST-STAGE EVAPORATOR
CONCENTRATED H_3PO_4
LP STEAM
HYDROFLUOSILICIC ACID
GYPSUM SLURRY TO POND
*TO SCRUBBER

FIGURE 4-2. FLOW DIAGRAM ILLUSTRATING A WET-PROCESS PHOSPHORIC ACID PLANT

Reproduced from best available copy.

The single-tank reactor (Dorr-Oliver design) illustrated in Figure 4-2 consists of two concentric cylinders. Reactants are added to the annulus and digestion occurs in this outer compartment. The second (central) compartment provides retention time for gypsum crystal growth and prevents short-circuiting of rock.

The Prayon reactor has been a widely used design. This process variation involves the use of a rectangular, multicompartment attack tank - typically 10 compartments - as indicated in Figure 4-3. The compartments are arranged in two adjacent rows with the first and tenth located at one end of the reactor and the fifth and sixth at the other. In operation, digestion of the rock occurs in the first four compartments, the next four provide retention time for the growth of gypsum crystals, the ninth supplies feed for the vacuum flash cooler, and the tenth receives the cooled slurry from the flash cooler and splits the flow between the filter and a recycle stream.

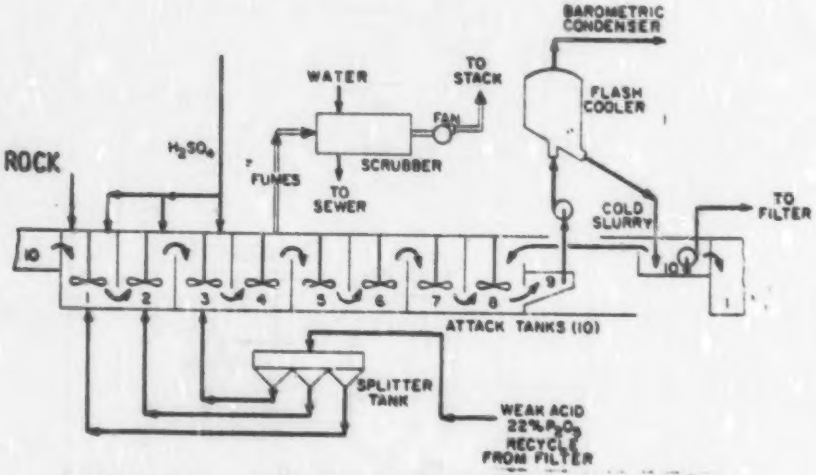

BAROMETRIC CONDENSER
WATER
TO STACK
FLASH COOLER
FAN
ROCK
H_2SO_4
FUMES
SCRUBBER
TO SEWER
COLD SLURRY
TO FILTER
10
1
2
3
4
5
6
7
8
9
10
1
ATTACK TANKS (10)
SPLITTER TANK
WEAK ACID $22\% P_2O_5$ RECYCLE FROM FILTER

FIGURE 4-3. FLOW DIAGRAM FOR PRAYON REACTOR[3]

Proper crystal growth depends on maintaining sulfate ion concentration within narrow limits at all points in the reaction slurry. The proper sulfate ion concentration appears to be slightly more than 1.5 percent. Lower levels give poor crystals that are difficult to filter; higher concentrations interfere with the reaction by causing deposition of calcium sulfate on unreacted rock.[4] Good reactor design will prevent sudden changes of sulfate ion concentration, will maintain the sulfate ion concentration and temperature near optimum, and will provide sufficiently long holdup time to allow growth of large, easily filterable crystals without the formation of excessive crystal nuclei.

Impurities in small amounts often have a marked effect on crystal growth when they are present in a medium where crystallization is taking place. Usually this impurity effect is detrimental. Such impurities are likely to cause crystal fragmentation, small crystal size, or a shift to needles or other hard-to-filter forms.

Concentrated sulfuric acid is usually fed to the reactor. If dilute acid is used, its water content must be evaporated later. The only other water entering the reactor comes from the filter-wash water. To minimize evaporation costs, it is important to use as little wash water as is consistent with practical P_2O_5 recoveries.

Considerable heat of reaction is generated in the reactor and must be removed. This is done either by blowing air over the hot slurry surface or by vacuum flash cooling part of the slurry and sending it back into the reactor. Modern plants use the vacuum flash cooling technique illustrated in Figures 4-2 and 4-3.

The reaction slurry is held in the reactor for up to 8 hours, depending on the type rock and the reactor design, before being sent to the filter. The most common filter design in use is the rotary horizontal tilting-pan vacuum filter shown in Figures 4-2 and 4-4. This type unit consists of a series of individual filter cells mounted on a revolving annular frame with each cell functioning essentially like a Buchner funnel. Figure 4-4 illustrates the operating cycle of a rotary horizontal tilting-pan filter.

Product slurry from the reactor is introduced into a filter cell and vacuum is applied. After a dewatering period, the filter cake undergoes 2 or 3 stages of washing with progressively weaker solutions of phosphoric acid. The wash-water flow is countercurrent to the rotation of the filter cake with heated fresh water* used for the last wash, the filtrate from this step used as the washing liquor for the preceding stage, etc.

After the last washing, the cell is subjected to a cake dewatering step and then inverted to discharge the gypsum. Cleaning of the filter media occurs at this time. The cell is then returned to its upright position and begins a new cycle.

* In many plants a heated barometric condenser water is used.

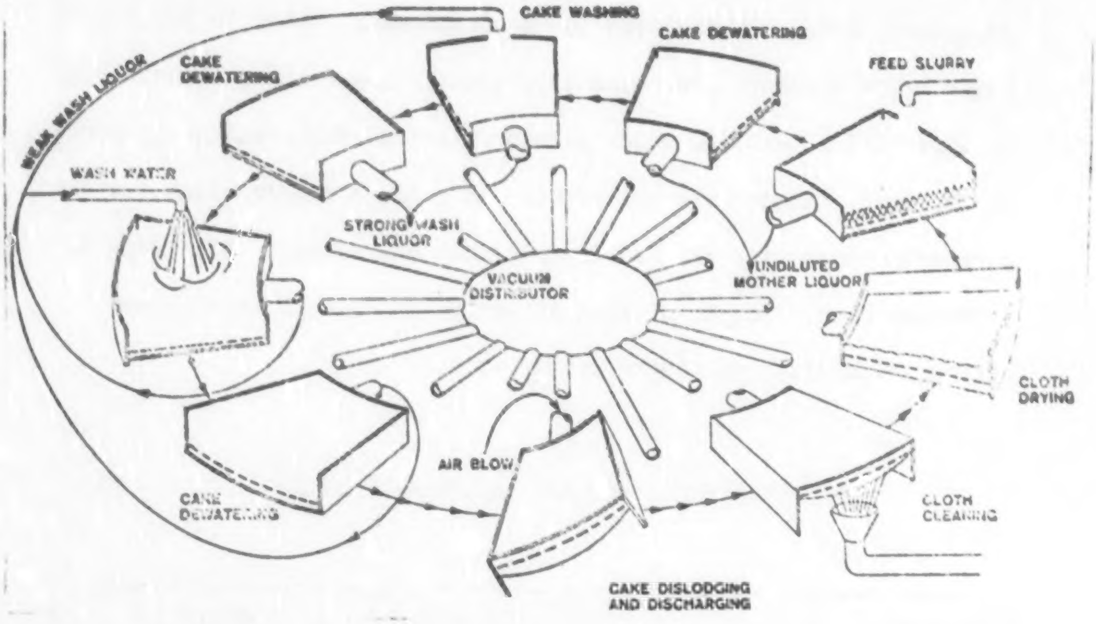

CAKE WASHING
CAKE DEWATERING
FEED SLURRY
WEAK WASH LIQUOR
CAKE DEWATERING
WASH WATER
STRONG WASH LIQUOR
VACUUM DISTRIBUTOR
UNDILUTED MOTHER LIQUOR
CLOTH DRYING
AIR BLOW
CAKE DEWATERING
CLOTH CLEANING
CAKE DISLODGING AND DISCHARGING

FIGURE 4-4. OPERATING CYCLE OF ROTARY HORIZONTAL TILTING PAN FILTER[5]

The 32 percent acid obtained from the filter generally needs concentrating for further use. Current practice is to concentrate it by evaporation in a two or three-stage vacuum evaporator system. Wet process acid is usually not concentrated above 54 percent, because the boiling point of the acid rises sharply above this concentration.[6] Corrosion problems also become more difficult when concentration exceeds 54 percent. In the evaporator, illustrated in Figure 4-2, provision is made for recovery of fluoride as fluosilicic acid. This recovery feature is not necessary to the evaporation and its inclusion is a matter of economics. Many evaporation plants have not installed this device.

Table 4-2 shows a typical analysis of commercial wet-process phosphoric acid. In addition to the components listed in Table 4-2, other trace elements are commonly present. Impurities, those listed in Table 4-2 as well as trace elements, affect the physical properties of the acid. Commercial wet-process acid has a higher viscosity than pure orthophosphoric acid of the same concentration. This tends to increase the difficulty of separating the calcium sulfate formed during acidulation of the phosphate rock.

TABLE 4-2

COMPONENTS OF TYPICAL WET-PROCESS ACID[7]

Component	Weight, %	Component	Weight, %
P_2O_5	53.4	Na	0.2
CA	0.1	K	0.01
Fe	1.2	F	0.9
Al	0.6	SO_3	1.5
Mg	0.3	SiO_2	0.1
Cr	0.01	C	0.2
V	0.02	solid	2.9
H_2O and other	37.56		

4.3 SUPERPHOSPHORIC ACID MANUFACTURE.

Superphosphoric acid (also referred to as polyphosphoric acid) is a mixture containing other forms of phosphoric acid in addition to orthophosphoric acid (H_3PO_4). At least one-third of the P_2O_5 content of superphosphoric acid are polyphosphates such as pyrophosphoric acid ($H_4P_2O_7$), tripolyphosphoric acid ($H_5P_3O_{10}$), tetrapolyphosphoric acid ($H_6P_4O_{13}$), etc. Pure orthophosphoric acid converts to polyphosphates when the P_2O_5 concentration exceeds 63.7 percent.[8] Concentrating above this level dehydrates orthophosphoric acid to form polyphosphates. Superphosphoric acid can have a minimum of 65 percent P_2O_5 which represents an orthophosphoric concentration of just over 100 percent. Commercial superphosphoric acid, made by concentrating wet-process or furnace orthophosphoric acid, normally has a P_2O_5 concentration between 72 and 76 percent.[8] Table 4-3 compares the properties of 76 percent superphosphoric acid to 54 percent orthophosphoric acid.

TABLE 4-3. COMPARISON OF ORTHOPHOSPHORIC TO SUPERPHOSPHORIC ACID[9]

	Orthophosphoric Acid	Superphosphoric Acid
Concentration of Commercial Acid, % P_2O_5	54	76
H_3PO_4 equivalent, %	75	105
Pounds P_2O_5/gal	7.1	12.2
Percent of P_2O_5 as Polyphosphates	0	51
Viscosity, CP		
at 100°F	12	400
at 200°F	4	45

Superphosphoric acid has a number of advantages over the more dilute forms of phosphoric acid, the foremost being economy in shipping. Since phosphoric acid of any concentration is usually transported at the same price per ton, a 40 percent savings in freight per unit weight of P_2O_5 results when superphosphoric acid is transported instead of ordinary phosphoric acid.[9] Superphosphoric acid may be diluted to orthophosphoric acid at its destination.

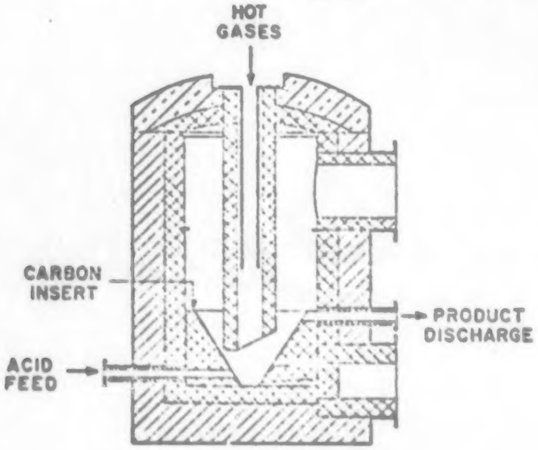
In addition to freight savings, superphosphoric acid offers several other advantages. It is less corrosive than orthophosphoric acid, which reduces storage costs. Finally, the conversion of wet-process acid has a special advantage. Unlike furnace acid, wet-process phosphoric acid contains appreciable quantities of impurities which continue to precipitate after manufacture and form hard cakes in pipelines and storage containers. When wet-process acid is converted to superphosphoric acid, the polyphosphates sequester the impurities and prevent their precipitation. Therefore shipment and storage of wet-process acid is far more attractive after conversion to superphosphoric acid.

Two commercial processes are used for the production of superphosphoric acid: submerged combustion and vacuum evaporation. The submerged combustion process was pioneered by the TVA; dehydration of the acid is accomplished by bubbling hot combustion gas through a pool of the acid.

The hot gases are supplied by burning natural gas in a separate chamber. The combustion gases are diluted with air to maintain a gas temperature of 1700°F for introduction into the acid evaporator. Figure 4-5 depicts an acid evaporator and Figure 4-6 the general process. After passage through the acid, the hot gases are sent to a separator to recover entrained acid droplets and then to emission control equipment.

Clarified acid containing 54 percent P_2O_5 is continuously fed to the evaporator from storage, and acid containing 72 percent P_2O_5 is withdrawn from the evaporator to product holding tanks. Cooling is accomplished by circulating water through stainless steel cooling tubes in the product tanks. The process can be controlled by regulating the natural gas and air flows to the combustion chamber, the dilution air to the combustion stream, or the amount of acid fed to the evaporator.

FIGURE 4-5. TVA EVAPORATOR FOR PRODUCING SUPERPHOSPHORIC ACID



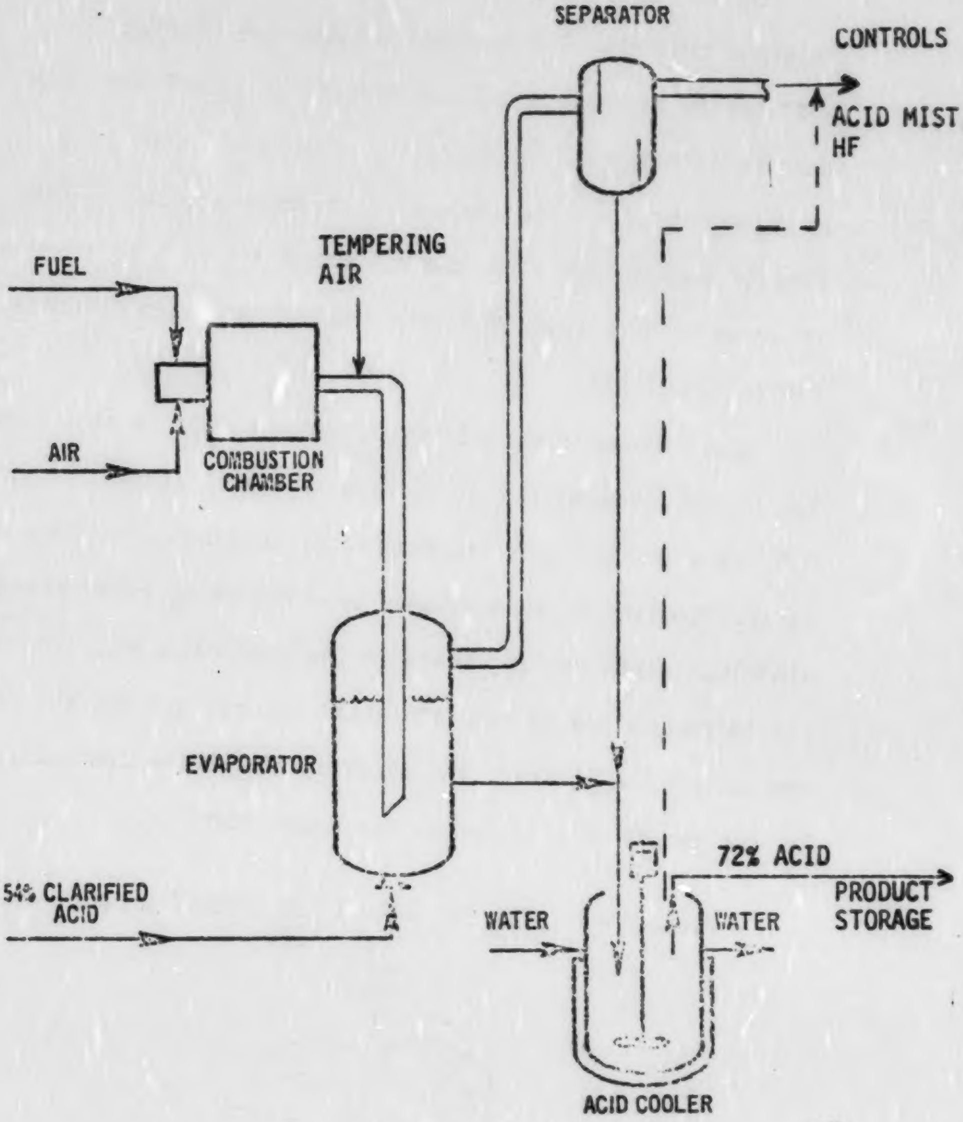

SEPARATOR
CONTROLS
ACID MIST, SiF_4
HF
TEMPERING AIR
FUEL
AIR
COMBUSTION CHAMBER
EVAPORATOR
54% CLARIFIED ACID
72% ACID
PRODUCT STORAGE
WATER
WATER
ACID COOLER

FIGURE 4-6. SUBMERGED COMBUSTION PROCESS FOR PRODUCING SUPERPHOSPHORIC ACID

In addition to the TVA process, a number of other submerged combustion processes have been developed. Among them are the Collier Carbon and Chemical Process, the Albright and Wilson Process, the Occidental Agricultural Chemicals Process, and the Armour Process. The latter process produces superphosphoric acid of about 83 percent P_2O_5 which is sometimes referred to as ultraphosphoric acid. The Occidental and TVA designs are currently in use in the United States.

Vacuum evaporation is by far the more important commercial method for concentrating wet-process phosphoric acid to superphosphoric acid. There are two commercial processes for the production of superphosphoric acid by vacuum evaporation:

1. The falling film evaporation process (Stauffer Chemical Co.) and
2. The forced circulation evaporation process (Swenson Evaporator Co.).

Feed acid clarification is required by both processes. Clarification is usually accomplished by settling or by a combination of ageing and settling.

In general, both processes are similar in operation. Both use high-vacuum concentrators with high-pressure steam to concentrate acid to 70 percent P_2O_5 and both introduce feed acid into a large volume of recycling product acid to maintain a highly concentrated process acid for lower corrosion rates. In both systems, product acid is pumped to a cooler before being sent to storage or shipped.

Figures 4-7 and 4-8 show the Stauffer and Swenson processes respectively. The Stauffer process adds 54 percent feed acid to the evaporator recycle tank where it mixes with concentrated product

FIGURE 4.7 STAUFFER EVAPORATOR PROCESS[10]

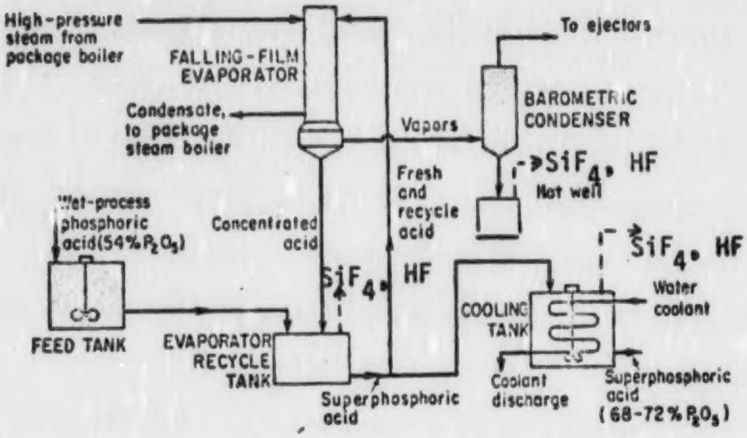
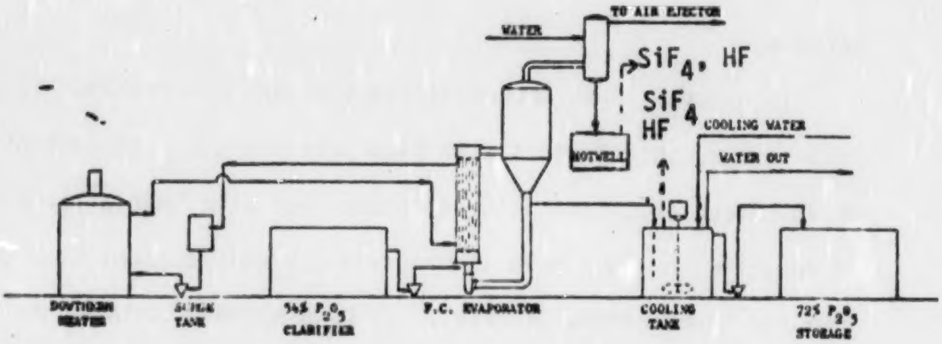

High-pressure steam from package boiler
FALLING-FILM EVAPORATOR
Condensate, to package steam boiler
Vapors
To ejectors
BAROMETRIC CONDENSER
SiF_4, HF
Hot well
Fresh and recycle acid
Concentrated acid
Wet-process phosphoric acid(54% P_2O_5)
SiF_4, HF
FEED TANK
EVAPORATOR RECYCLE TANK
Superphosphoric acid
SiF_4, HF
COOLING TANK
Water coolant
Coolant discharge
Superphosphoric acid (68-72% P_2O_5)

FIGURE 4-8 SWENSON EVAPORATOR PROCESS[10]


TO AIR EJECTOR
WATER
SiF_4, HF
SiF_4 HF
HOTWELL
COOLING WATER
WATER OUT
DOWTHERM HEATER
SURGE TANK
54% P_2O_5 CLARIFIER
F.C. EVAPORATOR
COOLING TANK
72% P_2O_5 STORAGE

acid. This mixture is pumped to the top of the evaporator and distributed to the inside wall of the evaporator tubes. The acid film moves down along the inside wall of the tubes receiving heat from the steam on the outside. Evaporation occurs and the concentrated acid is separated from the water vapor in a flash chamber located at the bottom of the evaporator. Product acid flows to the evaporator recycle tank and vapors to the barometric condenser. To insure minimum P_2O_5 loss, the separator section contains a mist eliminator to reduce carryover to the condenser.

The Swenson process, uses acid in the tube side of a forced circulation evaporator (Figure 4-8). Feed acid containing 54 percent P_2O_5 is mixed with concentrated acid as it is pumped into the concentrator system. As the acid leaves the heated tube bundle and enters the vapor head, evaporation occurs and the acid disengages from the water vapor. The vapor stream is vented to a barometric condenser while the acid flows toward the bottom of the vapor head tank where part of it is removed to the cooling tank and the remainder is recycled to the tube bundle.

4.4 DIAMMONIUM PHOSPHATE MANUFACTURE.

Diammonium phosphate is obtained by the reaction of ammonia with phosphoric acid. In addition to containing the available phosphate of triple superphosphate, diammonium phosphate has the advantage of containing 18 percent nitrogen from ammonia.

The importance of diammonium phosphate produced by wet-process acid has increased as it continues to replace normal superphosphate as a direct application material. The shift to diammonium phosphate is most evident on the supply side. Ammonium phosphate production now exceeds 2.7 million tons of P_2O_5 a year while normal superphosphate production has declined 32 percent since 1968 to 0.6 million tons.[11] Increasing amounts of diammonium phosphates are also being used in bulk blends as these increase in popularity.

The increased use of diammonium phosphate is attributable to several factors. It has a high water solubility, high analysis (18 percent nitrogen and 46 percent available P_2O_5), good physical characteristics, and low production cost. In addition, the phosphate content of diammonium phosphate (46 percent) is as high as triple-superphosphate, so by comparison, the 18 units of nitrogen can be shipped at no cost.

The TVA process for the production of diammonium phosphate appears to be the most favored with several variations of the original design now in use. A flow diagram of the basic process is shown in Figure 4-9.

Anhydrous ammonia and phosphoric acid (about 40 percent P_2O_5) are reacted in the preneutralizer using a NH_3 / H_3PO_4 mole ratio of 1.35. The primary reaction is as follows:

$$2\ NH_3 + H_3PO_4 \rightarrow (NH_4)_2\ HPO_4 \qquad (4\text{-}2)$$

The use of a 1.35 ratio of NH_3 / H_3PO_4 allows evaporation to a water

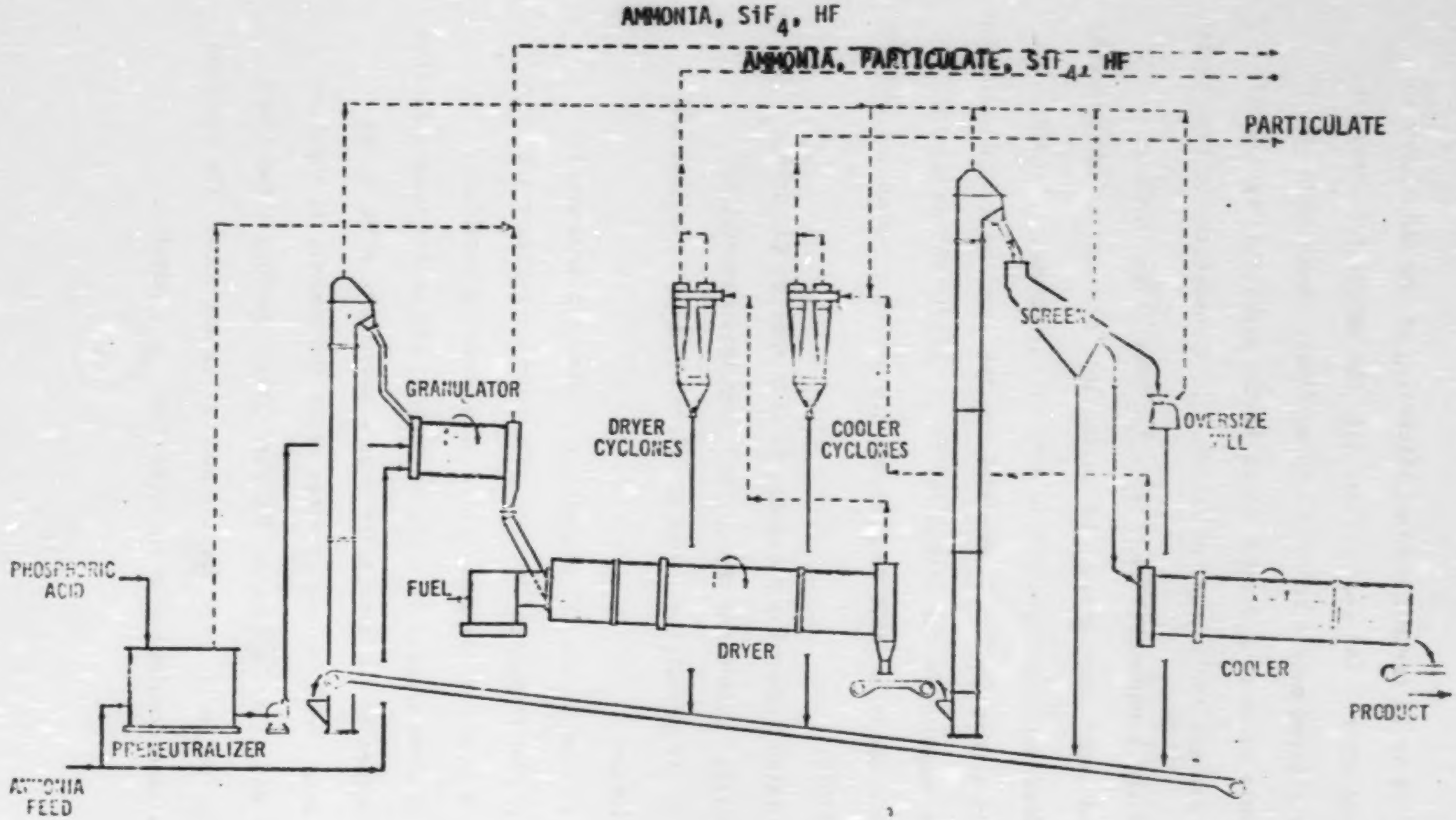

AMMONIA, SiF_4, HF
AMMONIA, PARTICULATE, SiF_4, HF
PARTICULATE
GRANULATOR
DRYER CYCLONES
COOLER CYCLONES
SCREEN
OVERSIZE MILL
PHOSPHORIC ACID
FUEL
DRYER
COOLER
PRODUCT
PRENEUTRALIZER
AMMONIA FEED

FIGURE 4-9. TVA DIAMMONIUM PHOSPHATE PROCESS.

content of 18 to 22 percent without thickening of the DAP slurry to a nonflowing state. The slurry flows into the ammoniator-granulator and is distributed over a bed of recycled fines. Ammoniation to the required mole ratio of 2.0 takes place in the granulator by injecting ammonia under the rolling bed of solids. It is necessary to feed excess ammonia to the granulator to achieve a 2.0 mole ratio. Excess ammonia and water vapor driven off by the heat of reaction are directed to a scrubber which uses phosphoric acid as the scrubbing liquid. The ammonia is almost completely recovered by the phosphoric acid scrubbing liquid and recycled to the preneutralizer. Solidification occurs rapidly once the mole ratio has reached 2.0 making a low solids recycle ratio feasible.

Granulated diammonium phosphate is next sent to the drier, then screened. Undersized and crushed oversized material are recycled to the granulator. Product sized material is cooled and sent to storage.

In addition to the TVA process, a single-step drum process designed by the Tennessee Corporation and the Dorr-Oliver granular process are used for the manufacture of diammonium phosphate. The single step drum process is designed so that the entire neutralization reaction occurs in the granulator drum - phosphoric acid is fed directly onto a rolling bed of fines while the ammonia is injected under the bed. In the case of the Dorr-Oliver design, a two-stage continuous reactor is used for the neutralization step. The reaction slurry is then combined with recycled fines in a pugmill.

4.5 TRIPLE SUPERPHOSPHATE MANUFACTURE AND STORAGE.

Triple superphosphate, also referred to as concentrated superphosphate, is a product obtained by treating phosphate rock with phosphoric acid. According to the grade of rock and the strength of acid used the product contains from 44 - 47 percent available P_2O_5.

Like diammonium phosphate, the importance of triple superphosphate has increased with the declining use of normal superphosphate. Triple superphosphate production now is around 1.7 million tons of P_2O_5 which is more than double that of normal superphosphate.[11] It is used in a variety of ways - large amounts are incorporated into high analysis blends, some are ammoniated, but the majority are applied directly to the soil.

4.5.1 Run-of-Pile Triple Superphosphate Manufacture and Storage

Figure 4-10 is a schematic diagram of the den process for the manufacture of run-of-pile triple superphosphate. Phosphoric acid containing 52 - 54 percent P_2O_5 is mixed at ambient temperature with phosphate rock which has been ground to about 70 percent minus 200 mesh. The majority of plants in the United States use the TVA cone mixer which is shown in Figure 4-11. This mixer has no moving parts and mixing is accomplished by the swirling action of rock and acid streams introduced simultaneously into the cone. The reaction that takes place during mixing is represented by the following equation:

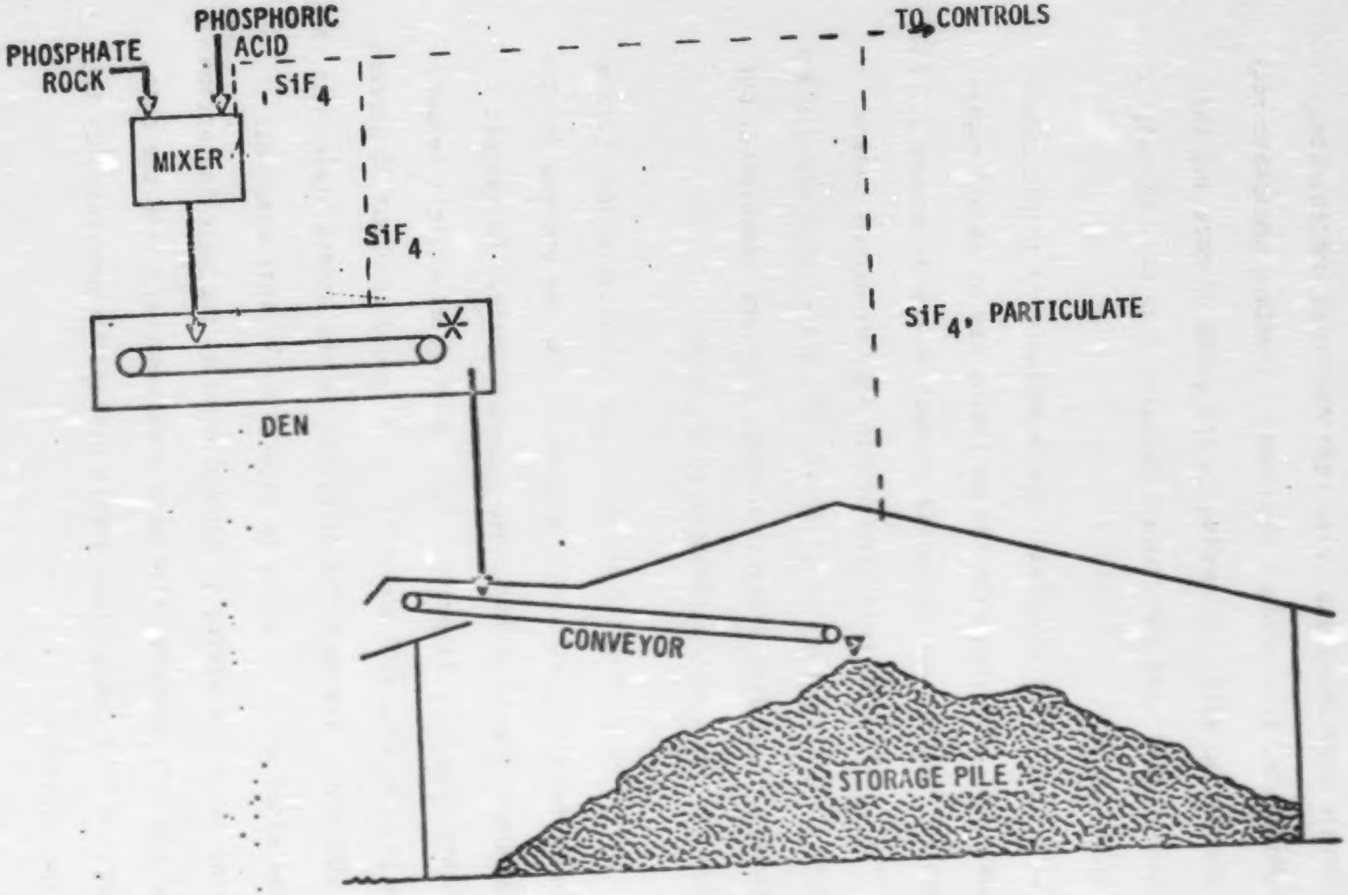
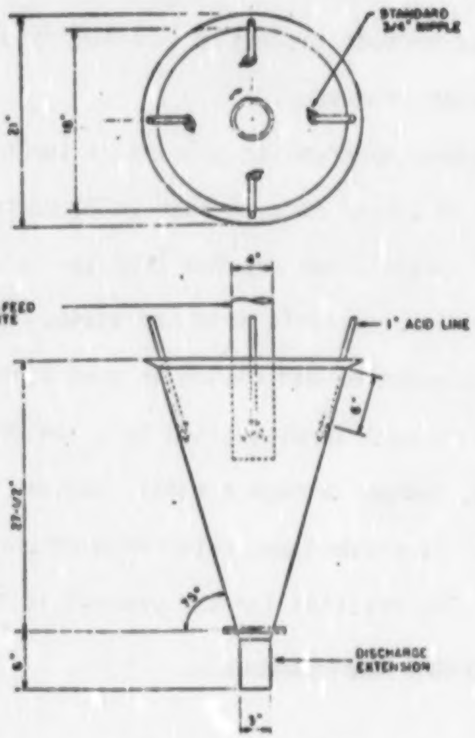

PHOSPHATE ROCK
PHOSPHORIC ACID
SiF_4
MIXER
SiF_4
TO CONTROLS
SiF_4, PARTICULATE
*
DEN
CONVEYOR
STORAGE PILE

FIGURE 4-10. RUN-OF-PILE TRIPLE SUPERPHOSPHATE PRODUCTION AND STORAGE

$$Ca_{10}(PO_4)_6F_2 + 14H_3PO_4 + 10H_2O \rightarrow 10CaH_4(PO_4)_2 \cdot H_2O + 2HF$$

After mixing, the slurry is directed to a "den" where solidification occurs. Like mixers, there are a number of den designs, one of the most popular continuous ones being the Broadfield. This den is a linear horizontal slat belt conveyor mounted on rollers with a long stationary box mounted over it and a revolving cutter at the end. The sides of the stationary box serve as retainers for the slurry until it sets up.

FIGURE 4-11. TVA CONE MIXER


STANDARD 3/4" NIPPLE
21"
18"
4"
ROCK FEED CHUTE
1" ACID LINE
6"
22-1/2"
75°
6"
DISCHARGE EXTENSION
3"

The solidified slurry which exits from the den is not a finished product. It must be cured - usually for 3 weeks or more - to allow the reactions to approach completion. The final curing stage is depicted in Figure 4-10 by the conveying of product to the sheltered storage pile.

4.5.2 Granular Triple Superphosphate Manufacture and Storage

Two processes for the direct production of granular triple superphosphate will be briefly presented. A third process uses cured run-of-pile triple superphosphate, treats it with water and steam in a rotary drum, then dries and screens the product. A large amount of granulated triple superphosphate is produced by this method but product properties are not as good as that produced by other processes.

The TVA one-step granular process is shown in Figure 4-12. In this process, phosphate rock, ground to 75 percent below 200 mesh, and recycled process fines are fed into the acidulation drum along with concentrated phosphoric acid and steam. The use of steam helps accelerate the reaction and ensure an even distribution of moisture in the mix. The mixture is discharged into the granulator where solidification occurs, passes through a rotary cooler, and is screened. Oversized material is crushed and returned with undersized material to the process. The reaction for the process is the same as that of run-of-pile triple superphosphate.

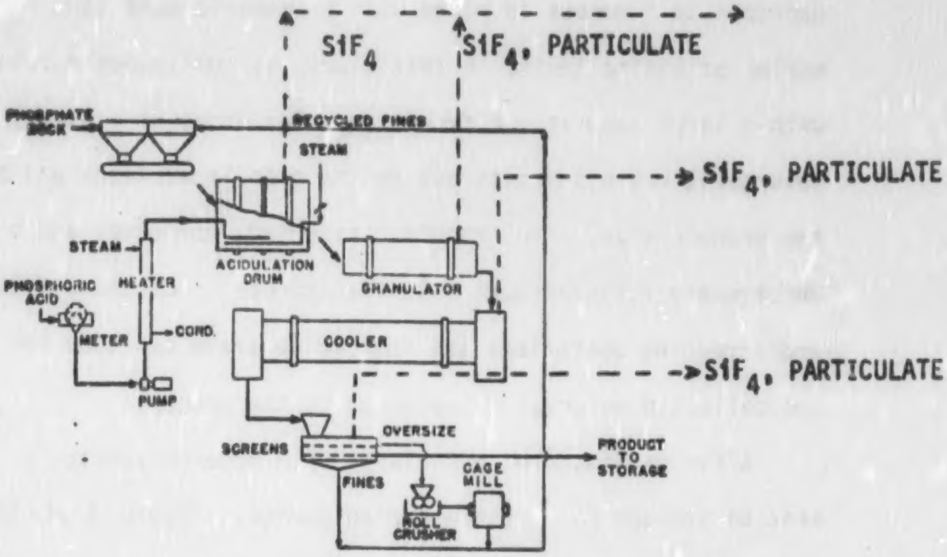

SiF_4
SiF_4, PARTICULATE
PHOSPHATE ROCK
RECYCLED FINES
STEAM
SiF_4, PARTICULATE
STEAM
ACIDULATION DRUM
PHOSPHORIC ACID
HEATER
GRANULATOR
METER
COND.
COOLER
PUMP
SiF_4, PARTICULATE
SCREENS
OVERSIZE
PRODUCT TO STORAGE
FINES
CAGE MILL
ROLL CRUSHER

FIGURE 4-12. TVA ONE-STEP PROCESS FOR GRANULAR TRIPLE SUPERPHOSPHATE

The Dorr-Oliver slurry granulation process is shown in Figure 4-13. In this process, phosphate rock, ground to an appropriate fineness is mixed with phosphoric acid (39% P_2O_5) in a series of mixing tanks. A thin slurry is continuously removed, mixed with a large quantity of dried, recycled fines in a pugmill mixer (blunger), where it coats out on the granule surfaces and builds up the granule size. The granules are dried, screened, and mostly (about 80 percent) recycled back into the process. Emissions from the drier and screening operations are sent to separate cyclones for dust removal and collected material is returned to the process.

After manufacture, granular triple superphosphate is sent to storage for a short curing period. Figure 4-14 illustrates the activities in the storage building. After 3 to 5 days,* during which some fluorides evolve from the storage pile, the product is considered cured and ready for shipping. Front-end loaders move the GTSP to elevators or hoppers where it is conveyed to screens for size separation. Oversize material is rejected, pulverized, and returned to the screen. Undersize material is returned to the GTSP production plant. Material within specification is shipped as product.

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* Many plants observe a shorter curing time.

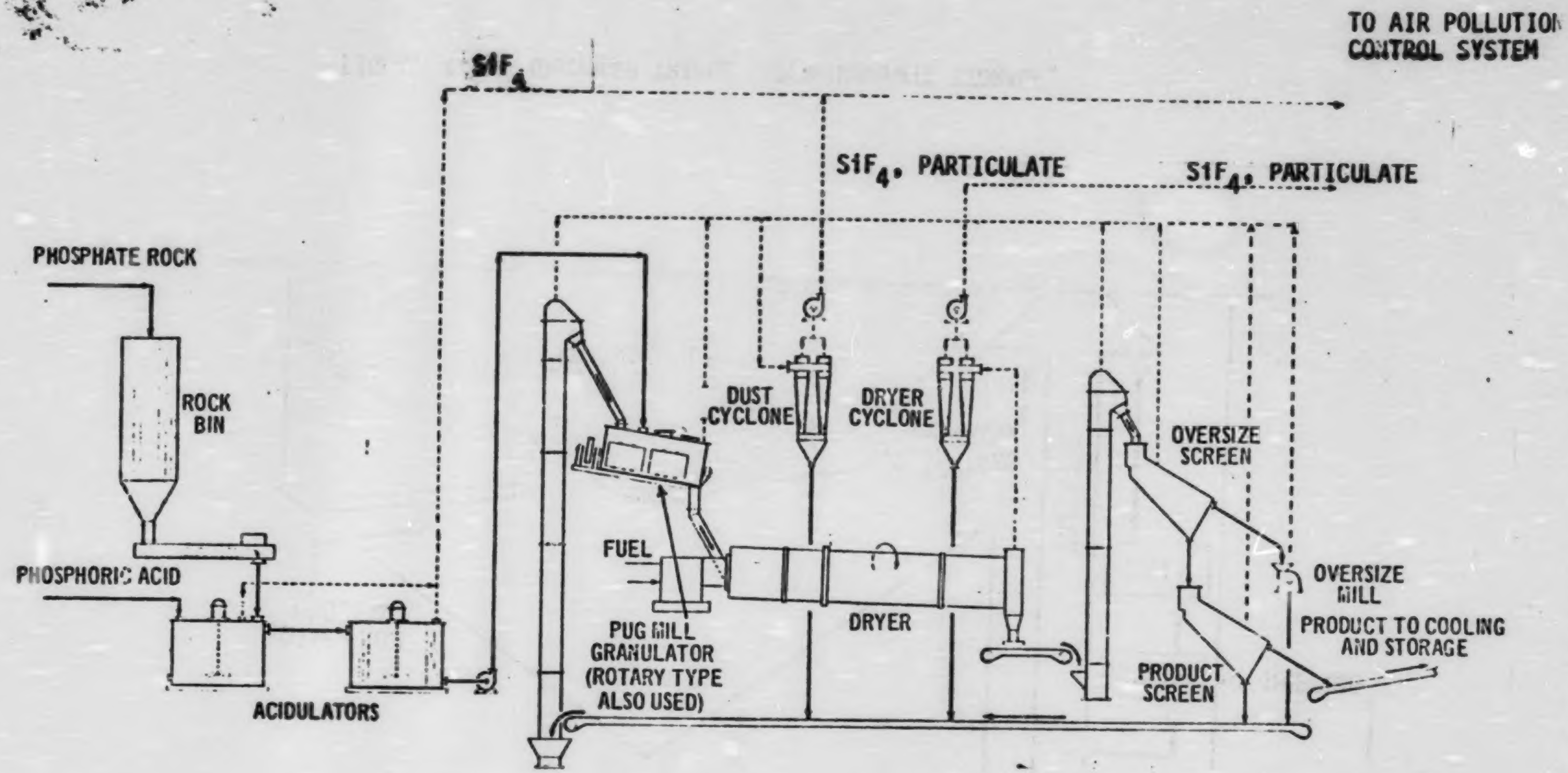
TO AIR POLLUTION
CONTROL SYSTEM
SiF_4
SiF_4, PARTICULATE
SiF_4, PARTICULATE
PHOSPHATE ROCK
ROCK BIN
PHOSPHORIC ACID
ACIDULATORS
DUST CYCLONE
DRYER CYCLONE
FUEL
PUG MILL GRANULATOR (ROTARY TYPE ALSO USED)
DRYER
OVERSIZE SCREEN
OVERSIZE MILL
PRODUCT TO COOLING AND STORAGE
PRODUCT SCREEN

FIGURE 4-13. DORR-OLIVER SLURRY GRANULATION PROCESS FOR TRIPLE SUPERPHOSPHATE

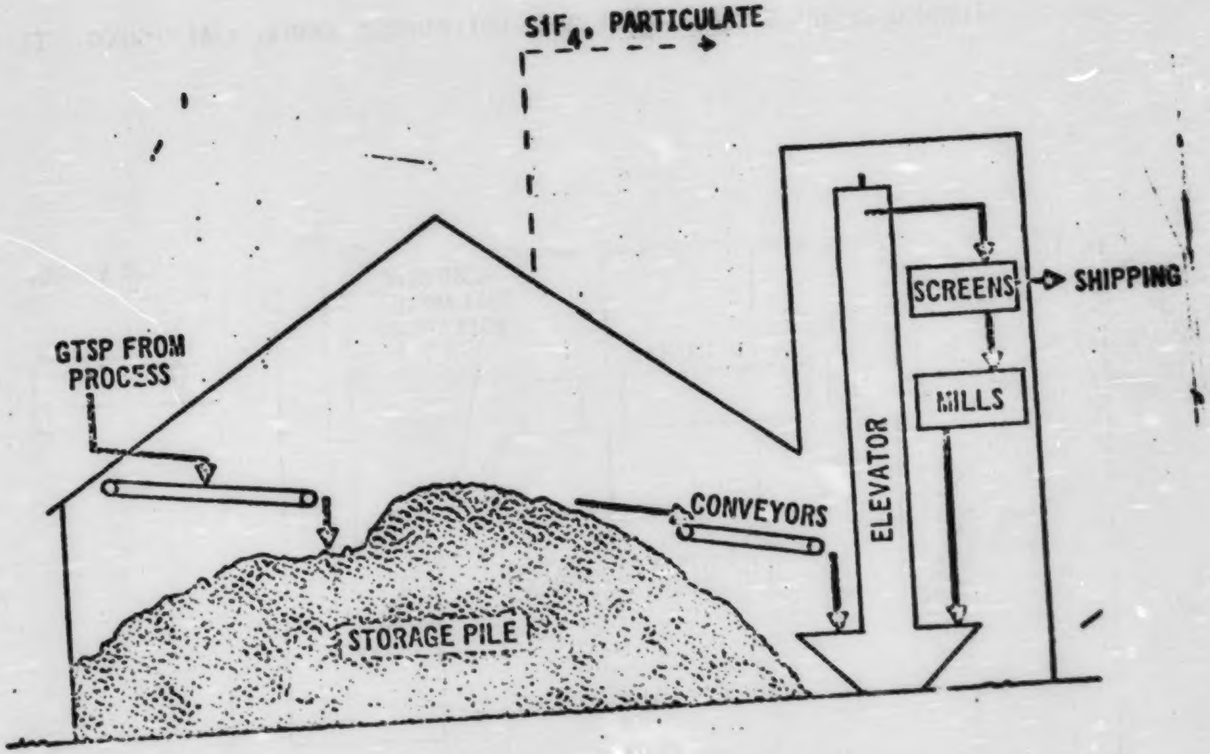
SiF_4, PARTICULATE
GTSP FROM PROCESS
SCREENS
SHIPPING
MILLS
ELEVATOR
CONVEYORS
STORAGE PILE

FIGURE 4-14. GRANULAR TRIPLE SUPERPHOSPHATE STORAGE.

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5. EMISSIONS

5.1 NATURE OF EMISSIONS.

In assessing the environmental effect of the emissions from the various phosphate fertilizer processes, fluorides - which are largely emitted in gaseous form, were considered to be the most significant and were chosen for regulation as discussed in Section 1.2.

Gaseous fluorides emitted from phosphate fertilizer processes are primarily silicon tetrafluoride (SiF_4) and hydrogen fluoride (HF)[1]. The origin of these gases may be traced to the reaction between phosphate rock and sulfuric acid represented by equation 4-1.

$$3Ca_{10}(PO_4)_6F_2 + 30H_2SO_4 + SiO_2 + 58H_2O \rightarrow 30CaSO_4 \cdot 2H_2O + 18H_3PO_4 + H_2SiF_6 \qquad (4\text{-}1)$$

Under the existing conditions of temperature and acidity, excess fluosilicic acid decomposes as follows:

$$H_2SiF_{6(l)} \rightarrow SiF_{4(g)} + 2HF_{(g)} \qquad (5\text{-}1)$$

Actually, the mole ratio of hydrogen fluoride to silicon tetrafluoride in the gases emitted during the decomposition of phosphate rock change with conditions (e.g., the amount of excess silica in the reaction mixture) and is seldom equal to the stoichiometric value. At high levels of excess silica, the hydrogen fluoride evolved will react to form silicon tetrafluoride according to equation 5-2:

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O \qquad (5\text{-}2)$$

At low concentrations of silica, emissions will be rich in hydrogen fluoride.

Not all of the fluorides are driven off during the digestion of the phosphate rock. A certain amount is retained in the product acid depending upon the type of rock treated and the process used. These fluorides can be emitted during the manufacture of superphosphoric acid, diammonium phosphate, or triple superphosphate.

Fluoride emissions from superphosphoric acid and diammonium phosphate processes depend solely on the fluoride content of the feed acid. In the manufacture of triple superphosphate, fluoride emissions can also be attributed to the release of fluorides from the phosphate rock. Calcium fluoride and silica in the rock react with phosphoric acid to form silicon tetrafluoride according to the following reaction[2]:

$$2CaF_2 + 4H_3PO_4 + SiO_2 \rightarrow SiF_4 + 2CaH_4(PO_4)_2 \cdot 2H_2O \qquad (5\text{-}3)$$

Scrubbing with water is an effective fluoride control technique because of the high water solubility of most gaseous fluorides.

This straight-forward approach is somewhat complicated, however, by the presence of silicon tetrafluoride. Silicon tetrafluoride will react with water to form hydrated silica ($Si(OH)_4$) and fluosilicic acid (H_2SiF_6) as indicated by equation 5-4:

$$3SiF_4 + 4H_2O \rightarrow 2H_2SiF_6 + Si(OH)_4 \qquad (5\text{-}4)$$

Hydrated silica precipitates forming deposits on control equipment surfaces which plug passageways and tend to absorb additional silicon tetrafluoride. The nature of the precipitate, in the presence of hydrogen fluoride, is temperature dependent. Below 125°F, the precipitate is in the form of a gel. Above this temperature, it is a solid.[3] Control systems should be designed to minimize plugging and to allow removal of silica deposits.

Entrainment of scrubbing liquid must be kept to a minimum to prevent the escape of absorbed fluorides. Fluorides can also be emitted as particulate from some fertilizer processes. Particulate emissions can be effectively controlled by using cyclones in combination with water scrubbers.

5.2 UNCONTROLLED FLUORIDE EMISSIONS.

5.2.1 Emissions from Wet-Process Phosphoric Acid Manufacture

Fluoride emissions from wet-process acid manufacture are gaseous silicon tetrafluoride and hydrogen fluoride. The reactor is the major source of fluoride emissions from the process accounting for as much as 90 percent of the fluorides emitted from an uncontrolled plant.[4] Additional sources are the filter, the filtrate feed and seal tanks, the flash cooler seal tank, the evaporator system hotwell, and the acid storage tanks. Table 5-1 lists reported emission factors for the various sources. Fluoride emissions will vary depending upon the type of rock treated and the process used.

Table 5-1 Fluoride Emissions from an Uncontrolled Wet-Process Phosphoric Acid Plant[4]

Source	Evolution Factor (lb TF/ton P_2O_5)
Reactor	0.04 - 2.2
Filter	0.01 - 0.06
Miscellaneous (filtrate feed and seal tanks, hotwells, etc.)	up to 0.26

Modern reactors emit fluorides from two sources; the reaction vessel and the vacuum flash cooler. The primary source is the reactor tank, where silicon tetrafluoride and hydrogen fluoride are evolved during the digestion of the phosphate rock.

To prevent an excessive temperature rise in the reactor, the heat of reaction is removed by cycling a portion of the reaction slurry through a vacuum flash cooler. Vapors from the cooler are condensed in a barometric condenser and sent to a hot well while the non-condensables are removed by a steam ejector and also vented to the hot well. This arrangement is illustrated in Figure 4-2. The majority of the fluorides evolved in the flash cooler are absorbed by the cooling water in the barometric condenser. If air cooling is utilized, fluoride evolution can be considerably greater than indicated in Table 5-1.

The filter is the second largest source of fluoride emissions. Most of the fluorides are evolved at the points where feed acid and wash liquor are introduced to the filter. These locations are usually hooded and vented to the digester scrubber.

A third source of fluoride emissions is the multiple effect evaporator used to concentrate the phosphoric acid from 30 percent P_2O_5 to 54 percent P_2O_5. It has been estimated that 20 to 40 percent of the fluorine originally introduced into the process with the rock is vaporized during this operation.[5] Most of these fluorides are collected in the system's barometric condensers. The remainder exit with the non-condensables and are sent to the hot well which becomes the emission source for this operation.

In the plant design illustrated in Figure 4-2, the vapor stream from the evaporator is scrubbed with a 15 to 25 percent solution of fluosilicic acid at a temperature at which water vapor, which would dilute the solution, is not condensed. The water vapor is then removed by a barometric condenser before the non-condensables are ejected from the system. Almost all of the fluoride is recovered as by-product fluosilicic acid.

In addition to the preceding sources of fluoride emissions, there are several minor sources. These include the vents from such points as sumps, clarifiers, and acid tanks. Collectively, these sources of fluoride emissions can be significant and are often ducted to a scrubber.

Table 5-2 illustrates a typical material balance for the fluorine originally present in phosphate rock. It should be noted that the results in any given wet-process acid plant may differ considerably from those shown in the table. Fluorine distribution will depend upon the type of rock treated, process used, and kind of operation prevailing.

TABLE 5-2
TYPICAL MATERIAL BALANCE OF FLUORIDE IN MANUFACTURE OF WET-PROCESS PHOSPHORIC ACID

Fluoride Input	# F/100 # Feed Rock
Feed	3.9
Fluoride Output	**# F/10C # Feed Rock**
Product acid	1.0
Gypsum	1.2
Barometric condensers	1.67
Air*	0.03
Total	3.9

*Typical emission from an uncontrolled plant.

Fluoride-bearing water from the barometric condensers as well as the gypsum slurry is sent to the gypsum pond. In the gypsum pond, silica present in the soil converts hydrogen fluoride to fluosilicates. Limestone or lime may be added to ponds to raise the pH and convert fluoride to insoluble calcium fluoride. Fluoride associated with the gypsum slurry is already in the insoluble form before being sent to the pond.

5.2.2 Emissions from Superphosphoric Acid Manufacture

5.2.2.1 Submerged combustion process

The direct contact evaporator is the major source of fluoride emissions from the submerged combustion process. Fluoride evolution is in the form of silicon tetrafluoride and hydrogen fluoride with a substantial portion as the latter.[6] The amount of fluorides evolved will depend on the fluoride content of the feed acid and the final concentration of phosphoric acid produced. Feed acid containing 54 percent P_2O_5 has a typical fluoride content (as F) of from 0.4 to 0.8 percent.[7]

Control of evaporator off-gases is complicated by the presence of large amounts of entrained phosphoric acid - amounting to as much as 5 percent of the P_2O_5 input to the concentrator.[8] An entrainment separator is used to recover acid and recycle it to the process. Some entrained acid exits the separator, however, and tends to form a difficult to control acid aerosol. The formation of this aerosol can be minimized by reducing the temperature of the combustion gases before they contact the acid.[9]

The acid sump and product holding tank are secondary sources of fluoride emissions from the submerged combustion process. These emission points are identified in Figure 4-6. Uncontrolled emissions from the submerged combustion process range from 13 to 22 pounds of fluoride per ton of P_2O_5 input.[10]

5.2.2.2 Vacuum evaporation process

The barometric condenser hotwell, the evaporator recycle tank, and the product cooling tank are the three sources of fluoride emissions from the vacuum evaporation process. These emission points are identified in Figures 4-7 and 4-8. Most of the fluorides evolved during evaporation are absorbed by the cooling water in the barometric condensers resulting in a negligible emission to the atmosphere from this source. Noncondensables are ejected from the condenser system and sent to the hotwell along with the condenser water. This results in the hotwell becoming the major source of emissions from the process. The evaporator recycle tank and the product cooling tank are lesser sources of fluoride emissions. Total emissions from an uncontrolled plant are estimated at 0.005 pounds per ton P_2O_5 input.[11]

5.2.3 Emissions from Diammonium Phosphate Manufacture.

Fluorides are introduced into the DAP process with the wet process phosphoric acid feed and are also evolved from the phosphoric acid scrubbing solution used to recover ammonia. Wet process acid which has been concentrated to 54 percent P_2O_5 typically contains 0.4 to 0.8 percent fluorides (as F) while filter acid (26-30% P_2O_5) will contain from 1.8 to 2.0 percent.[12,13] Phosphoric acid containing about 40 percent P_2O_5 - obtained by mixing 54 percent acid from the evaporators with filter acid - is usually used in the DAP process. Filter acid is used for ammonia recovery.

Major sources of fluoride emissions from diammonium phosphate plants include the reactor, granulator, dryer, cooler, screens and mills. The locations of these emission points are depicted in Figure 4-9. Ventilation streams from these sources are combined for purposes of control according to the following scheme: 1) reactor-granulator gases, 2) dryer gases, and 3) cooler and screening gases.

Fluorides and ammonia are the major emissions from both the reactor and the granulator. Reactor-granulator gases are treated for ammonia recovery in a scrubber that uses phosphoric acid as the scrubber liquid. The phosphoric acid reacts with the ammonia and the resulting product is recycled back to the process. Fluorides can be stripped from the phosphoric acid and a secondary scrubber is usually required for fluoride control. Removal of evolved fluorides can be complicated by their reaction with ammonia to form a particulate.

Drier emissions consist of ammonia, fluorides, and particulate. Gases are sent through a cyclone for product recovery before being treated for ammonia or fluoride removal. Additional fluorides can be stripped from the phosphoric acid scrubbing if ammonia recovery is practiced.

Emissions from the screens, mills, and cooler consist primarily of particulate and gaseous fluorides. All gases are treated for product recovery before entering fluoride control equipment. Evolution of fluorides from the production of diammonium phosphate is about 0.3 pounds of fluorides per ton of P_2O_5 from the reactor and granulator, and 0.3 pounds of fluoride per ton of P_2O_5 from the dryer, cooler and screens.[14]

5.2.4 Emissions from Triple Superphosphate Manufacture and Storage

5.2.4.1 Run-of-pile triple superphosphate

Fluorides can be released from both the phosphoric acid and the phosphate rock during the acidulation reaction. Major sources of fluoride emissions include the mixing cone, curing belt (den), transfer conveyors, and storage piles. These emission points are shown in Figure 4-10.

The mixing cone, curing belt, and transfer conveyors are typically hooded with ventilation streams sent to a common fluoride control system. Storage buildings are usually sealed and ventilated by approximately five air changes per hour.[15] The ventilation stream from the storage facility may either be combined with the mixer and den gases for treatment or sent to separate controls.

Fluoride emissions are primarily silicon tetrafluoride - from 35 to 55 percent of the total fluoride content of the acid and rock is volatilized as silicon tetrafluoride.[16] Major sources of fluoride are the mixing cone, curing belt, product conveyors, and storage facilities. Distribution of emissions among these sources will vary depending on the reactivity of the rock and the specific operating conditions employed. Emissions from the cone, curing belt, and conveyors can account for as much as 90 percent of the total fluorides released.[17] Conversely, it has been claimed that approximately 90 percent of the fluoride emissions from certain ROP plants are from the storage area. Emissions from the storage area depend on such factors as the turnover rate and the age and quantity of ROP-TSP in storage.

Evolution of fluorides from ROP-TSP production and storage has been estimated at 31 to 48 pounds per ton of P_2O_5. This estimate is based on the following assumptions: 1) silicon tetrafluoride is the only fluoride emitted in appreciable quantities and 2) the feed acid and rock contain typical amounts of fluorine.

5.2.4.2 Granular triple superphosphate

Manufacture

The major sources of fluoride emissions from granular triple superphosphate plants using the TVA one step process are the acidulation drum, the granulator, the cooler, and the screening and crushing operations. Major sources of emissions for the Dorr-Oliver process include the mixing tanks, the blunger, the drier, and the screens. These emission points are indicated in Figures 4-12 and 4-13. In addition to gaseous forms, fluorides are emitted as particulate from the granulator, blunger, dryer, screens, and mills.

The acidulation drum and granulator (TVA process) and the mixing tanks and blunger (Dorr-Oliver process) account for about 38 percent of the fluoride emissions, the drier and screens account for 50 percent, and the storage facilities account for the remainder.[18] It has been estimated that an uncontrolled production facility would emit approximately 21 [redacted] of fluorides per ton of P_2O_5 input.[18]

Storage

GTSP storage facilities can emit both particulate and gaseous fluorides. Uncontrolled emissions are estimated to be three pounds per ton of P_2O_5 input.[18]

5.3 TYPICAL CONTROLLED FLUORIDE EMISSIONS

5.3.1 Emissions from Wet-Process Phosphoric Acid Manufacture

Almost all existing wet-process phosphoric acid plants are equipped to treat the reactor and filter gases. A large number of installations also vent sumps, hotwells, and storage tanks to controls. Typical emissions range from 0.02 to 0.07 pounds of fluoride per ton of P_2O_5 input, however, emission factors as high as 0.60 pounds fluoride per ton P_2O_5 have been reported for a few poorly controlled plants.[19,20]

It is believed that approximately 53 percent of the wet-process acid plants - accounting for 74 percent of the production capacity - are either sufficiently controlled at present to meet the SPNSS emission level of 0.02 pounds of total fluorides (as F) per ton of P_2O_5 input to the process or will be required to attain that level by July 1975 to satisfy existing State regulations. This estimate is based on the following: 1) all wet-process acid plants located in Florida are required to meet an emission standard equivalent to the SPNSS as of July 1975 and 2) all wet process plants built since 1967 are assumed to have installed spray-crossflow packed bed scrubbers or their equivalent as a part of the original design.

5.3.2 Emissions from Superphosphoric Acid Manufacture

Two types of processes are used for superphosphoric acid manufacture; the vacuum evaporation (VE) process and the direct contact evaporation (DCE) or submerged combustion process. Emissions from the VE process are very low in comparison to the DCE process. Emissions from a VE process using a water actuated venturi to treat hotwell and product cooler vent gases have been reported to range from 4.1×10^{-4} to 15×10^{-4} pounds fluoride per ton P_2O_5 input.[21] However, uncontrolled emissions from this process are also less than the 0.01 pound per ton of P_2O_5 input emission guideline.

Since most of the existing superphosphoric acid plants use the VE process, approximately 78 percent of these plants are currently meeting the emission guideline.

Since the DCE process has much higher emissions, the emission guideline was established at 0.01 lb. F/ton P_2O_5 input. This guideline is consistent with the level of emission control achievable by application of best control equipment to a DCE process. Typical controls used are a primary scrubber for removal of entrained acid and one or more additional scrubbers for fluoride control.[22] Emission from an existing facility were reported at 0.12 pounds fluoride per ton P_2O_5.[23]

5.3.3 Emissions from Diammonium Phosphate Manufacture

Most existing plants are equipped with ammonia recovery scrubbers (venturi or cyclonic) on the reactor-granulator and drier streams and particulate controls (cyclones or wet scrubbers) on the cooler stream. Additional scrubbers for fluoride removal are common, but not typical. Only about 15-20 percent of the installations contacted by EPA during the development of the SPNSS were equipped with spray-crossflow packed bed scrubbers or their equivalent for fluoride removal. Fluoride emissions range from 0.06 to 0.5 pounds per ton P_2O_5 depending upon the degree of control provided.[24]

5.3.4 Emissions from Triple Superphosphate Manufacture and Storage

5.3.4.1 ROP triple superphosphate (manufacture and storage)

All run-of-pile triple superphosphate production facilities and 70 percent of the storage facilities are equipped with some form of control.[25] Emissions from those plants which control both production and storage areas can range from 0.2 to 3.1 pounds of fluoride per ton of P_2O_5 input depending upon the degree of control provided.[26,27] Plants with uncontrolled storage facilities could emit as much as 12.7 pounds of fluoride per ton of P_2O_5 input. At least 60 percent of the industry will be required to meet State emission standards equivalent to the SPNSS by July 1975.

5.3.4.2 Granular triple superphosphate (manufacture)

Existing State regulations will require 75 percent of the industry to meet an emission standard of 0.20 pound fluoride per ton P_2O_5 by July 1975. Emission factors for the industry range from 0.20 to 0.60 pounds per ton P_2O_5.[28]

5.3.4.3 Granular triple superphosphate (storage)

Approximately 75 percent of the GTSP storage facilities are thought to be equipped with some form of control.[29] Poorly controlled buildings can release as much as 15×10^{-4} pounds of fluoride per hour per ton of P_2O_5 in storage.[30] Well-controlled storage facilities can reduce emissions to less than 5×10^{-4} pounds fluoride per hour per ton of P_2O_5 in storage.[30] It is estimated that 33 percent of the controlled buildings could meet SPNSS emission level.[29]

5.4 GYPSUM POND EMISSIONS

A wet process phosphoric acid plant produces gypsum in slurry form, according to the chemical reaction indicated in equation 4-1. The reaction also volatilizes fluorides which are largely absorbed in scrubber and condenser water and is then sent with the gypsum to large storage ponds, known as gypsum ponds or "gyp" ponds. Over 70 percent of the fluorine content of the rock used in the wet-acid process may pass over to the gyp pond. If the same plant also produces DAP or TSP, a large part of the fluorine content of the phosphoric acid will also pass to the gyp pond through the use of water scrubbers in these additional processes. Thus, 85 percent or more of the fluorine originally present in the phosphate rock may find its way to the gyp pond.

The water of the gyp pond is normally acid, having a pH around 1.5. This acidity is probably due to inclusion of phosphoric acid in the washed gypsum from the gypsum filter. It is impractical to remove all of the acid from the filter cake by washing. For this reason, gyp ponds around the country have been found to have a fluoride concentration of 2000-12,500 ppm.[31-34] The fluoride concentration of a given pond does not continue rising, but tends to stabilize. This may be due to precipitation of complex calcium silicofluorides in the pond water.[35] There would be an equilibrium involving these complexes, hydrogen ion, and soluble or volatile dissolved fluorides.

It has been observed that the above concentrations of fluoride exert a partial pressure out of gyp pond water and that volatile fluorides tend to evolve from gyp ponds. Based on wet process phosphoric acid production, plants have gyp ponds of surface areas in the range of 0.1-0.4 acres per daily ton of P_2O_5.[34] This means that a large plant may have a gyp pond with surface area of 200 acres or more.

Emission factors have been estimated, measured and calculated for gyp ponds. These factors vary from about 0.2 to 10 lbs F/acre day.[31-34]

The most comprehensive work on gyp pond emission factors is that recently done in EPA Grant No. R-800950.[34] The experimental and mathematical procedures are quite detailed and the entire report should be examined by those needing to understand the methods used. The partial pressure of fluorides out of actual pond water was determined in the laboratory. The evaporation rates of dilute fluoride solutions were derived from known data for flat water surfaces, using established mass transfer principles. Also, ambient air fluorides were measured downwind of the same gyp ponds which furnished the above water samples for fluoride partial pressure measurements. Finally, the contribution of the gyp pond to the fluoride measurement at the downwind sensor was calculated, using a variant of the Pasquill diffusion equation. The source strength in this equation was, of course, calculated with the partial pressure data and mass transfer coefficient previously developed. There were a total of 95 useable downwind measurements for two pond sites, and the estimated and the measured downwind fluoride concentrations showed good agreement. The calculated value of the ambient air fluorine concentration downwind of the pond was found to be statistically the same as the measured value.

Some emission factors from the above investigation are given in Table 5-3. Data at other temperatures may be found in the original reference.

Table 5-3. FLUORIDE EMISSION FACTORS FOR SELECTED GYPSUM PONDS AT 90°F; lbs/acre day.[34]

	Wind velocity at 16 ft elevation, m/sec			
	1	2	4	6
Pond 10 6,400 ppm F	0.8	1.3	2.3	-
Pond 20 12,000 ppm F	0.8	1.3	2.3	3.2

For the two plants studied, the emission rates were nearly identical. There may be significant differences if other ponds are considered, but more measurements would be required to establish this.

The most effective way to reduce fluoride evolution from gyp ponds would be to reduce their fluoride partial pressure in some way. The most effective method now known would be liming, to raise the pH. Liming to a pH of 6.1 has reduced the partial pressure of fluoride 30-fold.[31] The indicated lime cost would be high for the case described, but this cost can be reduced if a method can be found to reduce phosphoric acid loss to the gyp pond.

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6. CONTROL TECHNIQUES FOR FLUORIDES FROM PHOSPHATE FERTILIZER PROCESSES

6.1 SPRAY-CROSSFLOW PACKED BED SCRUBBER

6.1.1 Description

The spray-crossflow packed bed scrubber has been accepted for several years as the most satisfactory fluoride control device available for wet-process phosphoric acid plants.[1] Most wet-process acid plants built since 1967 probably have installed this scrubber as part of the original design. During this same time, however, the spray-crossflow packed bed design has seen less general use in processes other than wet acid manufacture. The reluctance of the fertilizer industry to fully adopt the spray-crossflow packed bed scrubber can be traced primarily to concern about its operational dependability when treating effluent streams with a high solids loading. Such effluent streams can be handled by placing a venturi scrubber in series with and before a spray-crossflow packed bed scrubber; the EPA has tested a number of DAP and GTSP plants having this dual scrubber arrangement. Also, improvements in spray-crossflow packed scrubber design have alleviated the initial problem of plugging and allow a greater solids handling capacity. The development of stricter fluoride emission standards should provide incentive for more widespread use of this scrubber design.

Figure 6-1 is a diagrammatic representation of the spray-crossflow packed bed scrubber. It consists of two sections - a spray chamber and a packed bed - separated by a series of irrigated baffles. Scrubber size will depend primarily upon the volume of gas treated. A typical unit treating the effluent streams from a wet acid plant (20,000 scfm) is 9 feet wide, 10 feet high, and 30 feet long.[2]

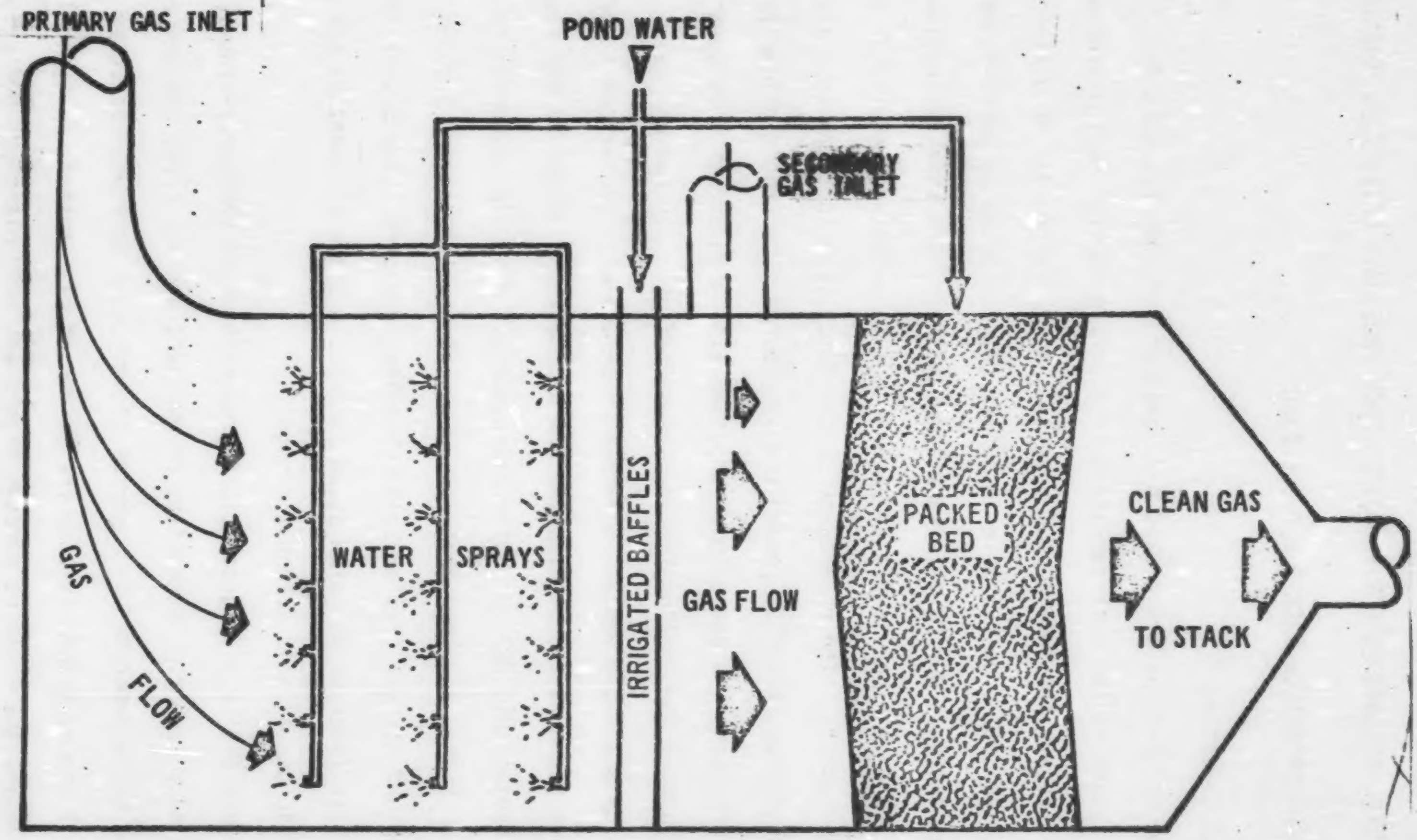

PRIMARY GAS INLET
POND WATER
SECONDARY GAS INLET
GAS FLOW
WATER SPRAYS
IRRIGATED BAFFLES
GAS FLOW
PACKED BED
CLEAN GAS
TO STACK

FIGURE 6-1. SPRAY-CROSSFLOW PACKED BED SCRUBBER.

All internal parts of the scrubber are constructed of corrosion resistant plastics or rubber-lined steel. Teflon can be used for high temperature service. General maintenance consists of replacement of the packing once or twice a year. Expected life of the scrubber is 20 years.

Both the spray and the packed section is equipped with a gas inlet. Effluent streams with relatively high fluoride concentrations - particularly those rich in silicon tetrafluoride - are treated in the spray chamber before entering the packing. This preliminary scrubbing removes silicon tetrafluoride thereby reducing the danger of plugging the bed. At the same time, it reduces the loading on the packed stage and provides some solids handling capacity. Gases low in silicon tetrafluoride can be introduced directly to the packed section.

The spray section accounts for approximately 40 to 50 percent of the total length of the scrubber. It consists of a series of countercurrent spray manifolds with each pair of spray manifolds followed by a system of irrigated baffles. The irrigated baffles remove precipitated silica and prevent the formation of scale in the spray chamber.

Packed beds of both cocurrent and crossflow design have been tried with the crossflow design proving to be the more dependable. The crossflow design operates with the gas stream moving horizontally through the bed while the scrubbing liquid flows vertically through the packing. Solids tend to deposit near the front of the bed where they can be washed off by a cleaning spray. This design also allows the use of a higher irrigation rate at the front of the bed to aid in solids removal. The back portion of the bed is usually operated dry to provide mist elimination.

The bed is seldom more than 3 or 4 feet in length, but this can be increased if necessary with little change in capital or operating cost.[1] Several types of ceramic and polyethylene packing are in use with Tellerettes probably the most common. Pressure loss through the scrubber ranges from 1 to 8 inches of water with 4 to 6 being average.[1,3]

Recycled pond water is normally used as the scrubbing liquid in both the spray and packed sections. Filters are located in the water lines ahead of the spray nozzles to prevent plugging by suspended solids. The ratio of scrubbing liquid to gas ranges from 0.02 to 0.07 gpm/acfm depending upon the fluoride content - especially the silicon tetrafluoride content - of the gas stream.[3,4] Approximately one-third of this water is used in the spray section while the remaining two-thirds is used in the packing.

The packed bed is designed for a scrubbing liquid inlet pressure of about 4 or 5 pounds-per-square-inch (gauge). Water at this pressure is available from the pond water recycle system. The spray section requires an inlet pressure of 20 to 30 pounds-per-square inch (gauge). This normally necessitates the use of a booster pump. Spent scrubbing water is collected in a sump at the bottom of the scrubber and pumped to the gypsum pond.

6.1.2 Emission Reduction

The use of gypsum pond water as the scrubbing solution complicates the task of fluoride removal regardless of the scrubber design. Gypsum pond water can be expected to contain from 0.2 to 1.5 percent fluosilicic acid (2000-12,500 ppm F) or most often, 5000-6000 ppm F.[5] Decomposition of fluosilicic acid to silicon tetrafluoride and hydrogen fluoride results in the formation of a vapor-liquid equilibrium that establishes a lower limit for the fluoride concentration of the gas stream leaving the scrubber. This limit will vary with the temperature, pressure, and fluosilicic acid concentration of the water. Table 6-1 presents equilibrium concentrations (y') calculated from experimentally obtained vapor pressure data at three temperatures and several fluosilicic acid concentrations.

Table 6-1. CALCULATED EQUILIBRIUM CONCENTRATIONS OF FLUORINE IN THE VAPOR PHASE OVER AQUEOUS SOLUTIONS OF FLUOSILICIC ACID[6]

Fluosilicic acid content of solution (wt %)	Total fluorine concentration in vapor phase (ppm F)		
	50°C	60°C	70°C
0.105	2.4	3.8	-
0.550	3.8	4.4[a]	10.5[a]
1.000	4.4	7.1	15.4
2.610	-	9.8[a]	20.7[a]
2.640	5.6	-	-
5.050	8.2[a]	14.2[a]	54.1[a]
7.470	12.4[a]	19.4[a]	208.5
9.550	13.5	25.6	-
11.715	19.1	34.6	-
14.480	-	83.5	-

[a] Average based on several vapor pressure measurements.

Providing that the solids loading of the effluent stream has been reduced sufficiently to prevent plugging, the fluoride removal efficiency of the spray-crossflow packed bed scrubber is limited only by the amount of packing used and the scrubbing liquid. Efficiencies as high as 98.5 and 99.9 percent have been measured for scrubbers installed at separate wet-process acid plants.[1,7] Table 6-2 lists the levels of fluoride control reached by several wet acid plants tested by the Environmental Protection Agency during the development of SPNSS. All plants used a spray-packed bed type scrubber to control the combined emissions from the reactor, the filter, and several miscellaneous sources and were felt to represent the best controlled segment of the industry. Gypsum pond water was used as the scrubbing liquid. Emission rates ranged from 0.002 to 0.015 pounds fluoride (as F) per ton P_2O_5 input to the process.

Table 6-2. SCRUBBER PERFORMANCE IN WET-PROCESS PHOSPHORIC ACID PLANTS[8]

Plant	Scrubber design	Fluoride emissions[a] (lb F/ton P_2O_5)
A	spray-cocurrent packed bed	0.015
B	spray-crossflow packed bed	0.006
C	spray-crossflow packed bed	0.002, 0.012[b]
D	spray-crossflow packed bed	0.011

[a] Average of testing results

[b] Second series of tests

Spray-packed bed type scrubbers have seen only limited service in diammonium phosphate and granular triple superphosphate plants and none at all in run-of-pile triple superphosphate plants. Table 6-3 presents performance data, collected during the development of SPNSS, for spray-crossflow packed bed scrubbers treating effluent streams from diammonium phosphate, granular triple superphosphate production, and granular triple superphosphate storage facilities. In most cases, a preliminary scrubber (venturi or cyclonic) was used to reduce the loading of other pollutants (ammonia or solids) prior to treatment in the spray-crossflow packed bed scrubber. Gypsum pond water was used as the scrubbing solution except where indicated. Fluoride emission rates from diammonium phosphate plants ranged from 0.029 to 0.039 pounds per ton P_2O_5 input, while emissions from granular triple superphosphate production facilities ranged from 0.06 to 0.18 pounds per ton P_2O_5. Granular triple superphosphate storage facility emissions were measured at 0.00036 pounds per hour per ton of P_2O_5 in storage.

6.1.3 Retrofit Costs for Spray-Crossflow Packed Bed Scrubbers

This section discusses the costs associated with retrofitting spray-crossflow packed bed scrubbers in wet-process phosphoric acid, superphosphoric acid, diammonium phosphate, run-of-pile triple superphosphate, and granular triple superphosphate plants. Two separate approaches - retrofit models and retrofit cases - are used to present cost information. The retrofit model approach is meant to estimate costs for an average or typical installation. No specific plant is expected to conform exactly to the description presented in these models. Where possible, the retrofit model treatment is supplemented by retrofit cases - descriptions of specific plants which have added spray-crossflow packed bed scrubbers to upgrade their original control systems.

Table 6-3. SPRAY-CROSSFLOW PACKED BED SCRUBBER PERFORMANCE IN DIAMMONIUM PHOSPHATE AND GRANULAR TRIPLE SUPERPHOSPHATE PLANTS[9]

Type of facility	Sources controlled	Primary controls	Secondary controls	Fluoride emissions[a] (lb F/ton P_2O_5)
DAP	reactor, granulator, drier, and cooler	3 venturi scrubbers in parallel[b]	3 spray-crossflow packed bed scrubbers in parallel	0.034, 0.029[c]
DAP	reactor, granulator, drier, and cooler	3 venturi scrubbers in parallel[b]	3 spray-crossflow packed bed scrubbers in parallel	0.039
GTSP	reactor, granulator, drier, and cooler	3 venturi scrubbers in parallel	3 spray-crossflow packed bed scrubbers in parallel	0.18, 0.06[c]
GTSP	reactor, granulator, drier, and cooler	process gases combined and sent to 2 venturi scrubbers in parallel followed by a cyclonic scrubber	spray-crossflow packed bed scrubber	0.21
GTSP storage	storage building	—	spray-crossflow packed bed scrubber	0.00036[d]

[a] Average of testing results.

[b] Weak phosphoric acid scrubbing solution.

[c] Second series of tests.

[d] Emission rate is in terms of pounds F per hour per ton of P_2O_5 in storage.

6.1.3.1 Retrofit Models

General Procedure

Each retrofit model provides the following information:

1. A brief description of the process in use,
2. A description of existing fluoride controls and the sources treated,
3. A description of the retrofit project (including the reduction in fluoride emissions achieved), and
4. A breakdown of estimated retrofit costs.

Items 1 and 2 are self-explanatory, however, items 3 and 4 will require some discussion. In the case of item 3, all retrofit systems are designed to meet SPNSS emission levels. A scaled plot plan of a model phosphate fertilizer complex was used to estimate piping, ductwork, pumps, and fan requirements.

The procedure used for development of costs is a module approach, starting with the purchase cost of an item - such as a pump, scrubber, fan, etc. - and building up to a field installed cost by using an appropriate factor to account for ancillary materials and labor.[10] For example, a pump of mild steel construction costing $10,000 is projected to $17,600 field installed. The installation cost index in this case is 1.76 and the installation cost is $7,600. If the pump were built of stainless steel, the purchase cost would be $19,300 but the installation cost would remain at $7,600 since it is calculated for the element of base construction - mild steel.

The purchase cost of the various items on an equipment specification list drawn up for each model plant were derived from literature, manufacturer's bulletins, telephone quotations from suppliers, and a report prepared by the Industrial Gas Cleaning Institute.[11] Scrubber costs were obtained by combining designer, manufacturer and user estimates. Purchase costs were scaled up to field installed costs by using an appropriate installed cost index. Table 6-4 is a list of the cost indices assumed for this analysis.

Table 6-4. INSTALLED COST INDICES

Item	Installed cost index
Pumps	1.76
Piping (except valves)	2.00
Scrubbers	1.20
Centrifugal fans	1.60
Stack	1.50
Ductwork	1.40

The sum of the field installed equipment cost is the direct cost billed to a particular project. Other costs such as general engineering, procurement of goods and services, equipmental rentals, field supervision, labor burdens, contractor fees, freights, insurance, sales taxes, and interest on funds used in construction are included in the catch-all category of indirect costs. In this study, the indirect cost is assumed to be 35 percent of the direct cost. In addition, a contingency factor is included in a capital project to account for unforeseen expenditures. Due to the nature of the type retrofit projects studied in this document, a factor of 25 percent of direct costs has been incorporated in the capital estimates. The total capital requirement of a project therefore is equal to the sum of the direct cost, the indirect cost, and the contingency cost, as indicated in equation 6-1:

$$I = D+0.35D+0.25D$$

where I = total capital

D = total direct cost

The following assumptions were used in the development of cost estimates:

1. The purchase costs of scrubbers were determined from the most recent manufacturer quotations, users wherever possible, and the Industrial Gas Cleaning Institute. The purchase cost of ductwork, stacks, and centrifugal fans were derived from a manufacturer's published list prices.[12] The costs are 1974 estimates based, for the most part, on the use of corrosion resistent fiber reinforced plastics (FRP) as the material of construction.
2. Installed costs for scrubbers, ductwork, stacks, and centrifugal fans (including drivers) were derived by multiplying the purchase costs by the appropriate cost index from Table 6-4. An inherent assumption is that FRP is a base

construction material suitable for application of the listed indices.

3. Demolition costs were estimated from contractor quotations to be $2500/8-hour day.

4. Piping costs were derived for a corrosion resistant material called Permastrand.

5. Pumps were assumed to be of stainless steel construction. Cost estimates were obtained from the literature.[13] These costs, originally published in 1968, were increased 54 percent (7.5% per year) to update to 1974 costs.

6. Costs for pump motors were obtained from the literature and adjusted for inflation using the same procedure described for pumps.[13]

7. Special compensatory factors for construction costs were incorporated into the ROP-TSP and GTSP storage facilities. Such factors appear under the headings of "sealing of storage building", "curing belt hooding", and "structural steel supports/bldg." The costs for these items were pro-rated on the basis of a recent engineering project study for a fertilizer producer.[14]

8. Cost for performance tests were based on a telephone survey of independent contractors.

9. Annualized Costs

a. Capital charges are 16.3 percent of the total capital outlay. This was derived from the capital recovery factor equation,

$$R = \frac{i\,(1 + i)^n}{(1 + i)^n - 1}\,P \qquad (6\text{-}2)$$

where: P = capital outlay (principal),

R = periodic capital charge,

i = annual interest rate (10%), and

n = number of payments (10)

b. Maintenance and repair charge were assumed to be 3 percent of the original investment.

c. Taxes, insurance, and administrative costs were assumed to be 4 percent of the original investment.

d. Operating labor costs were estimated at \$2,000 per year for the simple operation (phosphoric acid plant and GTS storage) \$4000 for the more difficult operations (DAP, ROP, and GTSP processing).[15]

e. Utilities (electricity only) were based on a rate of \$0.015 per kw-hr and 7,900 hours operation per year.

Wet Process Phosphoric Acid Plant

The model plant uses the Prayon process for the manufacture of wet process phosphoric acid. Figure 6-2 presents a basic flow diagram of the operation. The reactor is a multicompartment unit (9 compartments) with a designed production rate of 500 tons per day P_2O_5. Temperature control for the reactor is provided by a vacuum flash cooler. Under normal conditions, the reactor is maintained at a temperature of 160-180°F and produces an acid containing 30 percent P_2O_5.

Filtering and washing of the by-product gypsum is accomplished with a Bird-Prayon tilting pan filter. The separated gypsum is removed from the filter, slurried with water, and pumped to a settling pond. Product acid from the reactor (30% P_2O_5) is stored before being sent to the concentration system. Three vacuum evaporators in series are used to concentrate the acid to 54 percent P_2O_5. Evaporator off gases are treated in barometric condensers for removal of condensables; a large percentage of the fluorides are also collected.

Retrofit costs for some wet-process phosphoric acid plants could be substantially greater than those estimated for this plant. The retrofit model is of moderate complexity and includes all of the activities with which most installations are expected to become involved; however, increases in the gas volume being treated, additions to the scope of work, and space limitations are all factors capable of inflating the project cost above that estimated. Modifications to the plant drainage system and installation of a ventilation system

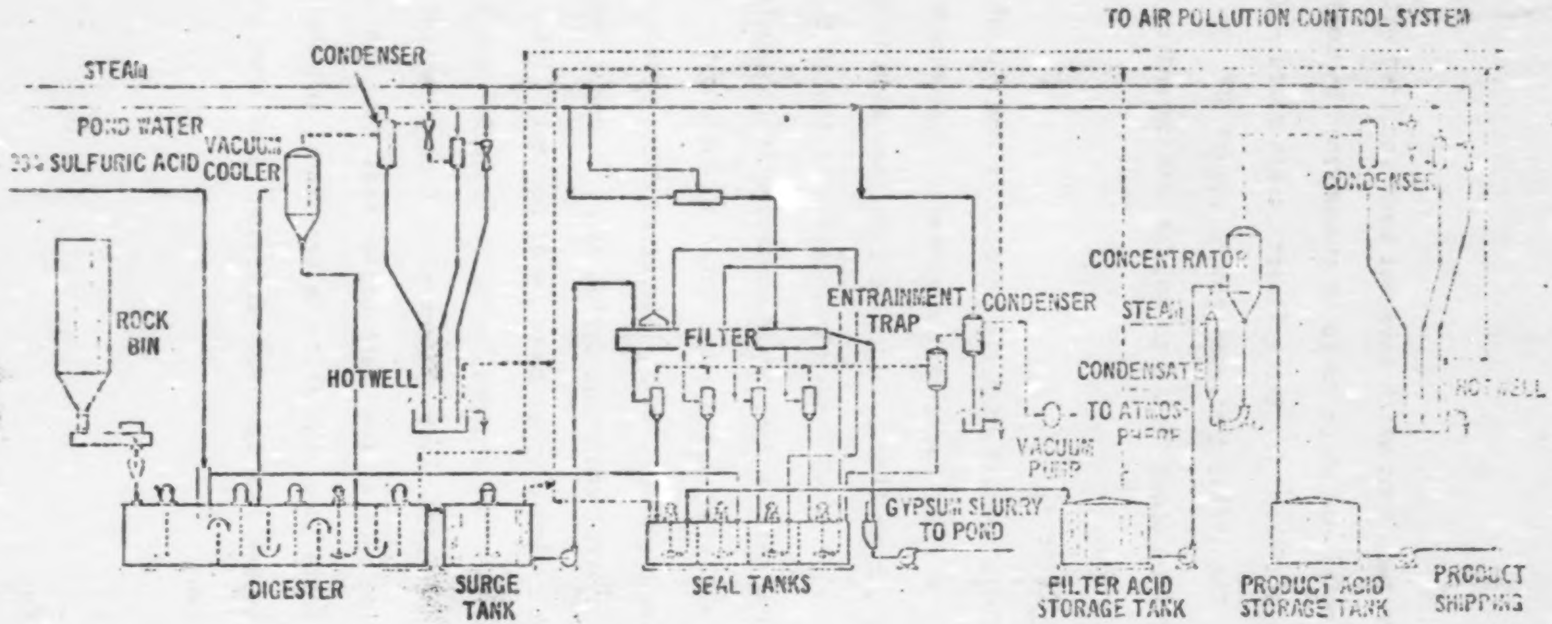

TO AIR POLLUTION CONTROL SYSTEM
STEAM
CONDENSER
POND WATER
30% SULFURIC ACID
VACUUM COOLER
ROCK BIN
HOTWELL
DIGESTER
SURGE TANK
FILTER
ENTRAINMENT TRAP
CONDENSER
SEAL TANKS
GYPSUM SLURRY TO POND
VACUUM PUMP
TO ATMOSPHERE
CONDENSATE
STEAM
CONCENTRATOR
CONDENSER
HOTWELL
FILTER ACID STORAGE TANK
PRODUCT ACID STORAGE TANK
PRODUCT SHIPPING

FIGURE 6-2. MANUFACTURE OF WET-PROCESS PHOSPHORIC ACID.

Reproduced from best available copy.

for the filter are two items which have not been included within the scope of the model but which could be encountered by some plants.

Costs will be estimated for two effluent stream sizes - 25,000 and 35,000 scfm. The effluent stream from an actual 500 ton per day plant could range from about 20,000 to 40,000 scfm depending primarily on the digester design.

Existing Controls (Case A)

Existing controls consist of a cyclonic spray tower used to treat the digester and the filter ventilation streams. Gypsum pond water is used as the scrubbing liquid. This scrubber has been in operation for eight years. Figure 6-3 shows the location of the unit.

Volumetric flow rates and fluoride concentrations associated with the various emission sources are listed in Table 6-5. The flow rates are based on a combination of literature data, source test information, and control equipment design data. Fluoride removal efficiency of the cyclonic spray tower is 81 percent. Total emissions to the atmosphere from the sources listed in Table 6-5 are 7.3 pounds of fluoride per hour with existing controls. Several miscellaneous sources of fluoride such as the flash cooler seal tank, the evaporator hotwell, the filtrate sump, the filtrate seal tank, and the filter acid storage tanks are uncontrolled. Emission rates from these sources are unknown.

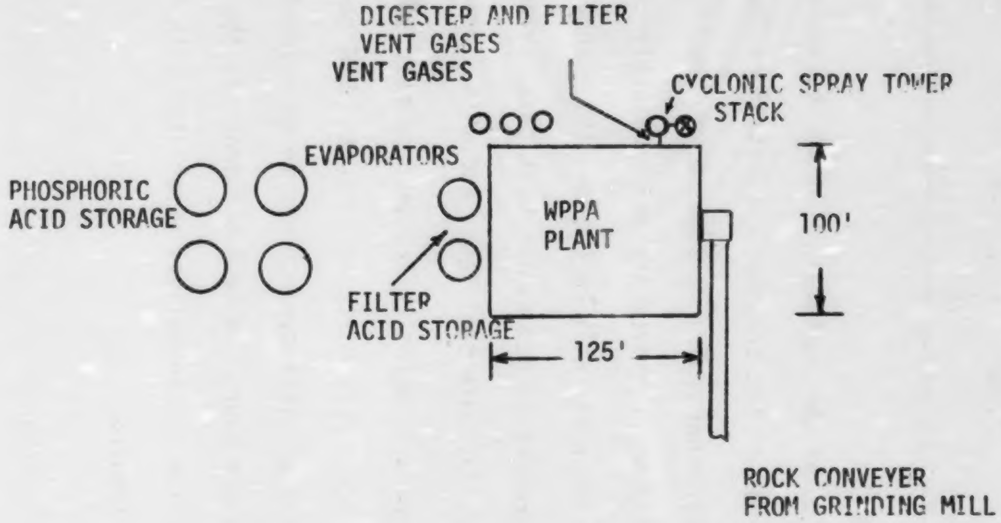

DIGESTER AND FILTER
VENT GASES
VENT GASES
CYCLONIC SPRAY TOWER
STACK
EVAPORATORS
PHOSPHORIC
ACID STORAGE
WPPA
PLANT
100'
FILTER
ACID STORAGE
125'
ROCK CONVEYER
FROM GRINDING MILL

Figure 6-3. EXISTING CONTROL EQUIPMENT LAYOUT FOR MODEL WPPA PLANT.

Table 6-5. FLOW RATES AND FLUORIDE CONCENTRATIONS OF WPPA PLANT EFFLUENT STREAMS SENT TO EXISTING CONTROLS (CASE A)

Emission source	Flow rate (SCFM)	Fluoride concentration[14] (mg/SCF)	(ppm)
Digester vent gas	10,000	25	1050
Filter vent gas	7,500	5.5	230

Retrofit Controls (Case A)

The retrofit consists of the replacement of the cyclonic spray tower with a crossflow packed bed scrubber. Limitations imposed by the arrangement of existing equipment require the new scrubber to be installed at a site 50 feet from the one previously occupied by the tower. Gypsum pond water will be used as the scrubbing liquid. Several miscellaneous sources (flash cooler seal tank, evaporator hot well, filtrate sump, filtrate seal tank, and acid storage tanks) will be vented to the new unit which is designed to meet SPNSS requirements for wet-process phosphoric acid plants (0.02 pounds fluoride per ton P_2O_5 input). This corresponds to an emission rate of 0.42 pounds fluoride per hour. Table 6-6 summarizes the volumetric flow rates and the fluoride concentrations associated with the emission sources to be treated.

Table 6-6. FLOW RATES AND FLUORIDE CONCENTRATIONS OF WPPA PLANT EFFLUENT STREAMS SENT TO RETROFITTED CONTROLS (CASE A)

Emission source	Flow rate, (SCFM)	Fluoride concentration[14]	
		(mg/SCF)	(ppm)
Digester vent gas	10,000	25	1050
Filter vent gas	7,500	5.5	230
Miscellaneous	7,500	0.3	13

Figure 6-4 provides a view of the plant layout following the completion of the retrofit project. Installation of the new scrubber requires the rearrangement of the existing ductwork and the addition of a new ventilation system to handle the miscellaneous sources. A new fan will be required for the digester-filter ventilation system because of the higher pressure drop of the crossflow packed bed scrubber. Treated gases will be exhausted from a newly installed 75-foot tall stack.

Scrubbing water will be obtained from existing plant water lines. A booster pump is required to provide 40 psig water for the spray section. Pond water is assumed to have the properties shown in Table 6-7. All scrubbing water will be recycled to the gypsum pond in the existing plant drainage system.

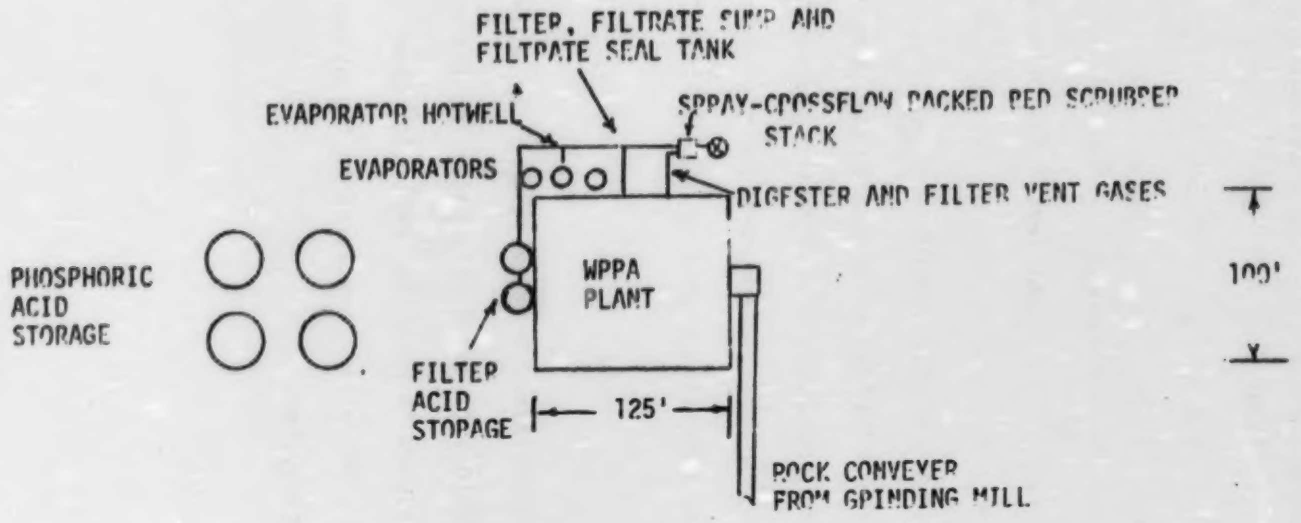

FILTER, FILTRATE SUMP AND
FILTRATE SEAL TANK
EVAPORATOR HOTWELL
SPRAY-CROSSFLOW PACKED BED SCRUBBER
STACK
EVAPORATORS
DIGESTER AND FILTER VENT GASES
PHOSPHORIC
ACID
STORAGE
WPPA
PLANT
100'
FILTER
ACID
STORAGE
125'
ROCK CONVEYER
FROM GRINDING MILL

FIGURE 6-4. RETROFIT CONTROL EQUIPMENT LAYOUT FOR MODEL WPPA PLANT.

Table 6-7. POND WATER SPECIFICATIONS[15]

	Design	Min.	Max.
Pond Water pH	2.0	1.2	2.2
Temp., °F	80.0	55	88
SO_4, wt %	0.15	-	-
P_2O_5, wt %	0.1	-	-
H_2SiF_6, wt %	0.63	0.25	1.0
Fluoride, wt %	0.5	0.2	0.8

Major retrofit items are listed in Table 6-8. All ducting, piping, and motors are specified in terms of the nearest appropriate standard size. Table 6-9 presents typical operating conditions for the new scrubber and the estimated number of transfer units (NTU) necessary to meet emission requirements. The NTU were calculated by using equation 6-3.

$$\text{NTU required} = \ln \frac{y_2 - y'}{y_1 - y'} \qquad (6\text{-}3)$$

where: y_2 = fluoride concentration of gas stream at the scrubber inlet

y_1 = fluoride concentration of gas stream at the scrubber outlet

y' = fluoride concentration of gas stream in equilibrium with entering liquid stream

Table 6-10 lists the estimated capital and annualized costs of the project.

Table 6-8. MAJOR RETROFIT ITEMS FOR MODEL WPPA PLANT (CASE A)

1. Ductwork required to connect existing digester-filter ventilation system with retrofit scrubber - 50 feet of 36-inch duct. New ventilation system connecting miscellaneous sources with control system. Requirements are - 175 feet of 9-inch duct, 50 feet of 10-inch duct, 125 feet of 12-inch duct, 75 feet of 16-inch duct, 100 feet of 20-inch duct, and 50 feet of 24-inch duct.

2. Pipe connecting spray-crossflow packed bed scrubber with existing plant water line - 150 feet of 6-inch pipe.

3. Booster pump for spray section - 190 gpm, 81 feet total dynamic head (TDH), 7.5 horsepower motor.

4. Centrifugal fan for digester - filter ventilation system - 17,500 scfm, 620 feet TDH, 50 horsepower motor. Fan for miscellaneous sources - 7,500 scfm, 660 feet TDH, 20 horsepower motor.

5. Removal of cyclonic spray tower and existing stack.

6. Spray-crossflow packed bed scrubber. Unit will be required to reduce the fluoride concentration to 0.13 mg/SCF (5.6 ppm) when using the pond water specified in Table 6-7 and treating the gases listed in Table 6-6.

7. Stack - 75-foot tall, 4-foot diameter.

Table 6-9. OPERATING CONDITIONS FOR SPRAY-CROSSFLOW PACKED BED SCRUBBER FOR MODEL WPPA PLANT, CASE A (500 tons/day P_2O_5)

Gas to Scrubber	
Flow, SCFM	25,000
Flow, DSCFM	22,725
Flow, ACFM	27,150
Temp., °F	116
Moisture, Vol. %	9.1
Fluoride (as F), lb/hr	38.7
Fluoride (as F), ppm	492
Gas from Scrubber	
Flow, SCFM	24,400
Flow, DSCFM	22,725
Flow, ACFM	25,700
Temp., °F	100
Moisture, Vol. %	6.5
Fluoride (as F), lb/hr	0.42
Fluoride (as F), ppm	5.6
Fluoride Removal, wt %	99
Estimated y', ppm (see page 6-5)	0.85
Estimated NTU required	4.7

Table 6-10. RETROFIT COSTS FOR MODEL WPPA PLANT, CASE 4 (500 tons/day P_2O_5) November 1974

	Cost ($)
A. Direct Items (installed)	
1. Spray-crossflow packed bed scrubber	58,900
2. Ductwork	18,600
3. Piping	2,400
4. Pumps and motor	4,200
5. Centrifugal fan and motor	14,300
6. Removal of old equipment	12,500
7. Stack	15,800
8. Performance test	4,000
Total Direct Items	130,700
B. Indirect Items	
Engineering construction expense, fee, interest on loans during construction, sales tax, freight insurance. (50% of A)	65,400
C. Contingency (25% of A)	32,700
D. Total Capital Investment	228,800
E. Annualized Costs	
1. Capital charges	37,300
2. Maintenance	6,200
3. Operating labor	2,000
4. Utilities	6.900
5. Taxes, insurance, administrative	9,100
Total Annualized Costs	61,500

Existing Controls (Case B)

The existing control system is the same as described in case A; a cyclonic spray tower is used to treat the digester and filter ventilation streams. Fluoride collection efficiency of the tower is 81 percent. Minor miscellaneous sources of fluoride are uncontrolled.

Volumetric flow rates and fluoride concentrations of the various effluent streams being controlled are listed in Table 6-11. Emissions from the sources listed are currently 11.0 pounds of fluoride per hour.

Table 6-11. FLOW RATES AND FLUORIDE CONCENTRATIONS OF WPPA PLANT EFFLUENT STREAMS SENT TO EXISTING CONTROLS (CASE B)

Emission Source	Flow Rate (SCFM)	Fluoride Concentration (mg/SCF)	(ppm)
Digester vent gas	20,000	20	840
Filter vent gas	7,500	5.5	230

Retrofit Controls (Case B)

Details of the retrofit project remain the same as in the initial case. The cyclonic spray tower treating the digester-filter gases will be replaced with a spray crossflow packed bed scrubber designed to handle the sources listed in Table 6-12.

Table 6-12. FLOW RATES AND FLUORIDE CONCENTRATIONS OF WPPA PLANT EFFLUENT STREAMS SENT TO RETROFITTED CONTROLS (CASE B)

Emission Source	Flow Rate (SCFM)	Fluoride Concentration (mg/SCF)	(ppm)
Digester vent gas	20,000	20	840
Filter vent gas	7,500	5.5	230
Miscellaneous	7,500	0.3	13

A list of major retrofit items is presented in Table 6-13 while operating conditions for the new scrubber are provided in Table 6-14. Estimated capital and annualized costs of the program is listed in Table 6-15. Increasing the capacity of the system by 10,000 SCFM has resulted in a 20 percent increase in the capital cost of the program and a 21 percent increase in the annualized cost.

Table 6-13. MAJOR RETROFIT ITEMS FOR MODEL WPPA PLANT (CASE B)

1. Ductwork required to connect existing digester-filter ventilation system with retrofit scrubber - 50 feet of 48-inch duct. New ventilation system connecting miscellaneous sources with control system - 175 feet of 9-inch duct, 50 feet of 10-inch duct, 125 feet of 12-inch duct, 75 feet of 16-inch duct, 100 feet of 20-inch duct, and 50 feet of 24-inch duct.

2. Pipe connecting spray-crossflow packed bed scrubber with existing plant water line - 150 feet of 8-inch pipe.

3. Booster pump for spray section - 269 gpm, 81 feet total dynamic head (TDH), 10 horsepower motor.

4. Centrifugal fan for digester - filter ventilation system - 27,500 scfm, 604 feet TDH, 75 horsepower motor. Fan for miscellaneous sources - 7,500 scfm, 660 feet TDH, 20 horsepower motor.

5. Removal of cyclonic spray tower and existing stack.

6. Spray-crossflow packed bed scrubber. Unit will be required to reduce the fluoride concentration to 0.09 mg/scf (3.9 ppm) when using the pond water specified in Table 6-7 and treating the gases listed in Table 6-11.

7. Stack - 75 foot tall, 5 foot diameter.

Table 6-14. OPERATING CONDITIONS FOR SPRAY-CROSSFLOW PACKED BED SCRUBBER FOR MODEL WPPA PLANT, CASE B (500 tons/day P_2O_5)

Gas to Scrubber	
Flow, SCFM	35,000
Flow, DSCFM	31,800
Flow, ACFM	37,600
Temp., °F	109
Moisture, vol. %	9.1
Fluoride (as F), lb/hr	58.1
Fluoride (as F), ppm	529
Gas from Scrubber	
Flow, SCFM	34,000
Flow, DSCFM	31,800
Flow, ACFM	35,600
Temp., °F	95
Moisture, vol. %	6.5
Fluoride, lb/hr	0.42
Fluoride, ppm	3.9
Fluoride removal, wt %	99.3
Estimated y', ppm	0.85
Estimated NTU required	5.2

Table 6-15. RETROFIT COSTS FOR MODEL WPPA PLANT, CASE B
(500 tons/day P_2O_5) November 1974

	Cost ($)
A. Direct Items (installed)	
1. Spray-crosslow packed bed scrubber	78,800
2. Ductwork	20,000
3. Piping	3,300
4. Pump and motor	5,300
5. Centrifugal fans and motors	16,000
6. Removal of old equipment	12,500
7. Stack	15,800
8. Performance test	4,000
Total Direct Items	155,700
B. Indirect Items	
Engineering construction expense, fee, interest on loans during construction, sales tax, freight insurance. (50% of A)	77,900
C. Contingency (25% of A)	38,900
D. Total Capital Investment	272,500
E. Annualized Costs	
1. Capital charges	44,400
2. Maintenance	7,500
3. Operating labor	2,000
4. Utilities	9,300
5. Taxes, insurance, administrative	10,900
Total Annualized Costs	74,100

Superphosphoric Acid

Two processes are currently available for the manufacture of superphosphoric acid - vacuum evaporation and submerged combustion. All but two of the existing U.S. production facilities use the vacuum evaporation process and it is believed that new facilities will favor vacuum evaporation. No retrofit model will be presented for vacuum evaporation plants because the low level of fluoride emissions from these facilities do not require control equipment in order to meet the emission guidelines.

Existing submerged combustion plants are expected to continue operation with some expansion in capacity possible. Retrofitted control equipment may be needed to meet the emission guidelines for this type of process. A retrofit model is presented for a plant using the submerged combustion process in order to estimate the costs of applying control equipment. The costs are developed based upon control equipment designed to meet the fluoride emission guideline of 0.01 pounds per ton of P_2O_5 input.

The model plant uses the Occidental Agricultural Chemicals process for the production of superphosphoric acid. Designed production capacity is 300 tons per day P_2O_5. Figure 4-6 is a basic flow diagram of the process.

Wet-process acid containing 54 percent P_2O_5 is fed to the evaporator and concentrated product acid containing 72 percent P_2O_5 is withdrawn. The acid is maintained at its boiling point by introducing a stream of hot combustion gases into the acid pool. Gaseous effluent from the evaporator is cooled by direct contact with weak phosphoric acid feed in the evaporator vapor outlet duct, treated for phosphoric acid recovery, given additional cooling, and treated for fluoride removal.

Existing Controls

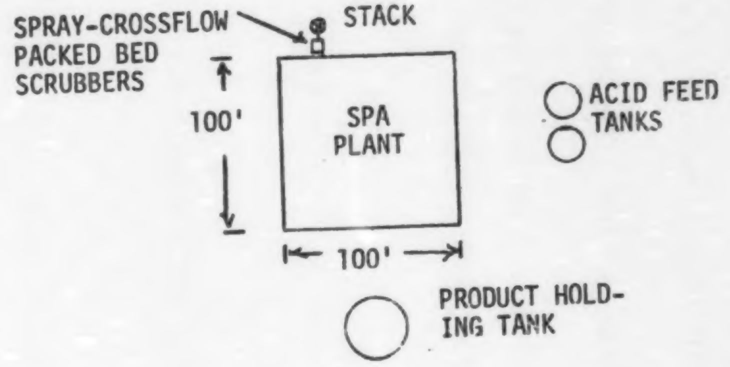
Exhaust gases from the evaporator are treated for the recovery of entrained acid before being sent to fluoride controls. The phosphoric acid recovery system consists of an initial cyclonic separator followed by a baffled spray duct and a second cyclonic separator. Weak phosphoric acid (30% P_2O_5) is used as the scrubbing liquid in the spray duct.

Fluoride controls consist of 3 spray chambers in series followed by an impingement scrubber. The spray chambers are baffled and each is followed by an entrainment separator. Pond water is used as the scrubbing liquid in all cases. Emissions to the atmosphere are 1.56 pounds of fluoride per hour with existing controls.[16]

Retrofit Controls

The retrofit cost projection is based on replacement of the impingement scrubber with a spray-crossflow packed bed scrubber. Since available space is usually limited, the new unit is assumed to be installed at the site previously occupied by the impingement scrubber. Figure 6-5 provides a schematic diagram of the plant following completion of the retrofit project.

Gypsum pond water will be used as the scrubbing liquid. Pond water characteristics are listed in Table 6-7. Retrofitted controls are designed to reduce fluoride emissions to 0.01 pounds fluoride/ton P_2O_5.


SPRAY-CROSSFLOW
PACKED BED
SCRUBBERS
STACK
100'
SPA
PLANT
100'
ACID FEED
TANKS
PRODUCT HOLDING TANK

□ — SPRAY-CROSSFLOW PACKED BED SCRUBBER

Figure 6-5. RETROFIT CONTROL EQUIPMENT LAYOUT FOR MODEL SPA PLANT

Installation of the spray-crossflow packed bed scrubber will require moderate alteration of existing ductwork and construction of a new pipe line connecting the scrubber to the existing water supply. No additional fans will be required. Treated gases will be exhausted from the existing stack. Scrubbing water is to be recycled to the gypsum pond in the existing drainage system.

A list of major items required for the retrofit project is presented in Table 6-16. Table 6-17 provides operating conditions for the new scrubber. Retrofit cost estimates are listed in Table 6-18.

Table 6-16. MAJOR RETROFIT ITEMS FOR MODEL SPA PLANT

1. Ductwork - modification of existing ducting to connect new spray-crossflow packed bed scrubber. Requirements are 100 feet of 30-inch duct.
2. Line connecting scrubber to main pond water supply system - 150 feet of 4-inch pipe.
3. Centrifugal pump - 130 gpm, 113 feet total dynamic head (TDH), 7.5 horsepower motor.
4. Removal of impingement scrubber.
5. Supports and foundations.
6. Spray-crossflow packed bed scrubber. Unit is required to reduce the fluoride concentration to 0.09 mg/SCF (4 ppm) when using pond water specified in Table 6-7 and treating gas stream described in Table 6-12.

Table 6-17. OPERATING CONDITIONS FOR SPRAY-CROSSFLOW PACKED BED SCRUBBER FOR MODEL SPA PLANT (300 Tons/Day P_2O_5)

Gas to Scrubber	
Flow, SCFM	9,800
Flow, DSCFM	9,110
Flow, ACFM	10,600
Temp., °F	115
Moisture, vol. %	7.0
Fluoride (as F), lb/hr	3.9
Fluoride (as F), ppm	126
Gas from Scrubber	
Flow, SCFM	9,400
Flow, DSCFM	9,110
Flow, ACFM	9,760
Temp., °F	90
Moisture, vol. %	3.0
Fluoride (as F), lb/hr	0.12
Fluoride (as F), ppm	4.0
Fluoride removal, wt %	96.7
Estimated y', ppm	0.85
Estimated NTU required	3.7

Table 6-18. RETROFIT COSTS FOR MODEL SPA PLANT (300 tons/day P_2O_5) November 1974

	Cost ($)
A. Direct Items (installed)	
1. Spray-crossflow packed bed scrubber	37,500
2. Ductwork	5,000
3. Piping	1,900
4. Pump and motor	4,200
5. Removal of old equipment	12,500
6. Performance test	4,000
Total Direct Items	64,300
B. Indirect Items	
Engineering construction expense, fee, interest on loans during construction, sales tax, freight insurance. (50% of A)	32,600
C. Contingency (25% of A)	16,300
D. Total Capital Investment	114,000
E. Annualized Costs	
1. Capital charges	18,600
2. Maintenance	3,000
3. Operating labor	2,000
4. Utilities	700
5. Taxes, insurance, administrative	4,400
Total Annualized Costs	28,700

Diammonium Phosphate

This plant uses the TVA process for the production of diammonium phosphate. A flow diagram of the operation is provided in Figure 4-9. The model plant has a designed production capacity of approximately 1080 tons per day diammonium phosphate (500 T/D P_2O_5).

A preneutralization reactor is used for the initial contacting of the anhydrous ammonia and the phosphoric acid. Completion of the reaction and solidification of the product occurs in the granulator. Effluent gases from the preneutralization reactor and the granulator are treated for ammonia recovery and fluoride control before being vented to the atmosphere.

A gas-fired rotary drier is used to remove excess moisture from the product. Drier flue gases are vented through dry cyclones for product recovery before being treated for ammonia removal. Air streams vented from accessory cooling and screening equipment are treated for particulate removal in dry cyclones before being exhausted.

Existing Controls

Exhaust gases from the preneutralization reactor and the granulator are combined and vented to a venturi scrubber for ammonia recovery. Weak phosphoric acid (30% P_2O_5) serves as the scrubbing liquid. Approximately 95 percent of the ammonia is recovered and recycled to the reactor. Fluorides stripped from the phosphoric acid in the venturi are removed by a cyclonic spray tower using gypsum pond water as the absorbing solution. Fluoride removal efficiency is 74 percent.

The drier flue gases are treated for product recovery before being sent to additional controls. Collected particulate is recycled to the granulator. A venturi scrubber using weak phosphoric acid is used for ammonia recovery. Ammonia removal efficiency is approximately 94 percent. No additional scrubbing is practiced.

Air streams vented from product cooling and screening equipment are sent through dry cyclones for product recovery, combined, and treated in a venturi scrubber for particulate removal. Weak phosphoric acid serves as the scrubbing solution. Collected DAP is recycled to the reactor. Diammonium phosphate particulate collected in dry cyclones is recycled to the granulator; that collected in the scrubber is recycled to the reactor.

Volumetric flow rates and fluoride concentrations associated with the three major emission sources are presented in Table 6-19. The values listed are estimates based on source test results and data obtained from a recent contract study of control equipment costs (5). Fluoride concentrations presented for the reactor-granulator and the drier gas streams are values at the outlet of the ammonia recovery scrubbers. Total fluoride emissions from the sources identified in Table 6-19 are 4.95 pounds per hour with existing controls.

Table 6-19. FLOW RATES AND FLUORIDE CONCENTRATIONS FOR DAP PLANT EMISSION SOURCES[17,18]

Emission source	Flow rate (SCFM)	Fluoride concentration (mg/SCF)	(ppm)
Combined reactor-granulator vent gases	30,000	0.65	27
Drier gases	45,000	0.36	15
Cooler and screening equipment vent gases	45,000	0.36	15

Retrofit Controls

The retrofit consists of the replacement of the cyclonic spray tower on the reactor-granulator stream with a spray-crossflow packed bed scrubber and the addition of spray-crossflow packed bed scrubbers as tail gas units to the drier and cooler streams. Gypsum pond water will be used as the scrubbing liquid. Pond water is available at 80°F with the properties listed in Table 6-7. The control system is designed to conform with the fluoride emission guideline of 0.06 pounds of fluoride per ton P_2O_5 input - 1.25 pounds fluoride per hour.

Existing controls are located as depicted in Figure 6-6. The arrangement of equipment is such that the spray-crossflow packed bed scrubbers can be installed adjacent to the venturi scrubbers after moderate alteration of the ductwork. A new water line must be installed to satisfy the increased demand caused by the retrofitted scrubbers. A new fan will also be required for both the drier and the cooler stream to compensate for the pressure drop of the secondary scrubber. Treated gases will be exhausted from the existing stack. Spent scrubbing water is to be recycled in the existing drainage system.

Figure 6-7 provides a view of the plant layout after the installation of new controls. A list of major retrofit items is provided in Table 6-20. Table 6-21 presents operating conditions for the spray-crossflow packed bed scrubbers. Total capital cost and annualized cost estimates for the project are presented in Table 6-22.

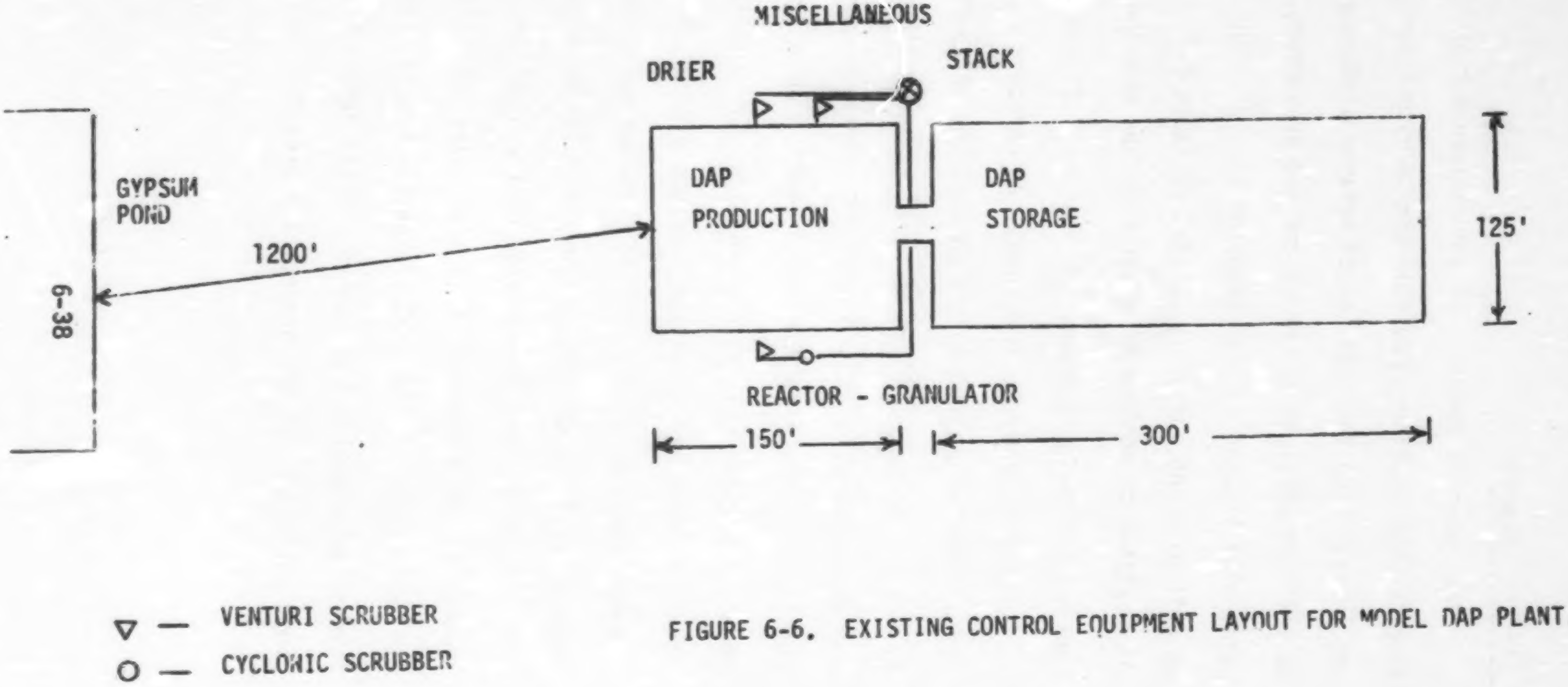

MISCELLANEOUS
DRIER
STACK
GYPSUM POND
1200'
DAP PRODUCTION
DAP STORAGE
125'
REACTOR - GRANULATOR
150'
300'
▽ — VENTURI SCRUBBER
○ — CYCLONIC SCRUBBER

FIGURE 6-6. EXISTING CONTROL EQUIPMENT LAYOUT FOR MODEL DAP PLANT.

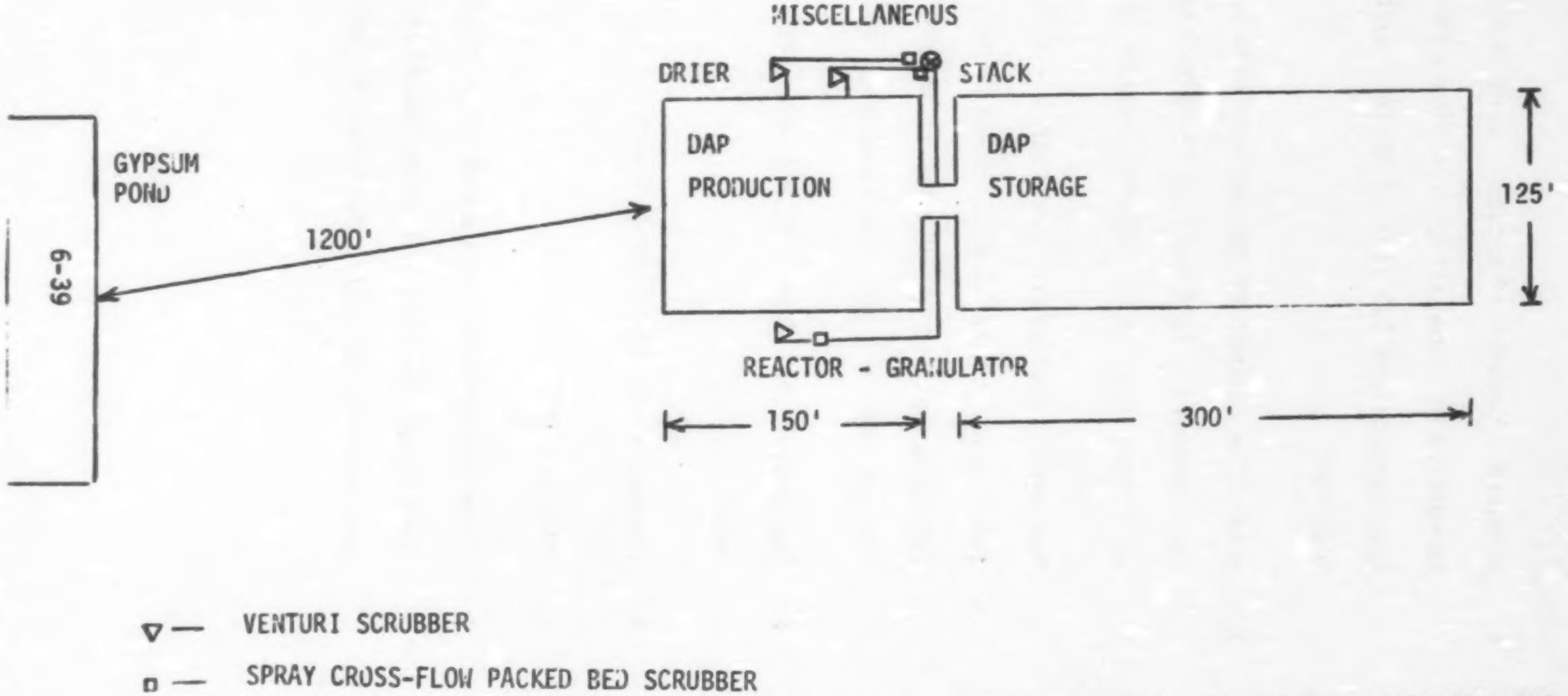

MISCELLANEOUS
DRIER
STACK
GYPSUM
POND
DAP
PRODUCTION
DAP
STORAGE
1200'
125'
REACTOR - GRANULATOR
150'
300'
▽ — VENTURI SCRUBBER
□ — SPRAY CROSS-FLOW PACKED BED SCRUBBER

FIGURE 6-7. RETROFIT CONTROL EQUIPMENT LAYOUT FOR MODEL DAP PLANT.

Table 6-20. MAJOR RETROFIT ITEMS FOR MODEL DAP PLANT

1. Ductwork - removal of cyclonic spray tower from service and connection of three spray-crossflow packed bed scrubbers. Requirements are 100 feet of 60-inch duct and 50 feet of 54-inch duct.

2. Water line connecting gypsum pond with spray-crossflow packed bed scrubbers - 1200 feet of 16-inch pipe with a 200-foot branch of 14-inch pipe and a 150-foot branch of 6-inch pipe.

3. Two centrifugal pumps (one spare) - 2550 gpm, 105 feet total dynamic head (TDH), 125 horsepower motor. Booster pump for spray section of both the drier and the cooler stream scrubber - 345 gpm, 89 feet TDH, 7.5 horsepower motor.

4. Two centrifugal fans - 45,000 scfm, 285 feet TDH, 50 horsepower motor.

5. Removal of cyclonic spray tower.

6. Supports and foundations.

7. Three spray-crossflow packed bed scrubbers. When using specified pond water and treating gases described in Table 6-19, scrubbers are required to obtain performance indicated in Table 6-21.

Table 6-21. OPERATING CONDITIONS FOR SPRAY-CROSSFLOW PACKED BED SCRUBBERS FOR MODEL DAP PLANT (500 Tons/Day P_2O_5)

	Reactor-granulator stream	Dryer stream	Cooler stream
Gas to scrubber			
Flow, SCFM	30,000	45,000	45,000
Flow, DSCFM	18,000	29,200	43,600
Flow, ACFM	34,000	52,700	49,600
Temp., °F	140	160	125
Moisture, vol. %	40	35	3
Fluoride (as F), lb/hr	2.58	2.14	2.14
Fluoride (as F), ppm	27.1	15.0	15.0
Gas from scrubber			
Flow, SCFM	19,400	31,500	45,400
Flow, DSCFM	18,000	29,200	43,600
Flow, ACFM	23,600	38,400	48,000
Temp., °F	100	100	100
Moisture, vol. %	7	7	4
Fluoride (as F), lb/hr	0.44	0.36	0.45
Fluoride (as F), ppm	5.9	3.0	3.0
Fluoride removal, wt %	83	83.5	79
Estimated y', ppm	1.05	1.25	1.05
Estimated NTU required	1.69	2.06	1.94

Table 6-22. RETROFIT COSTS FOR MODEL DAP PLANT (500 tons/day P_2O_5) November 1974

	Costs ($)
A. Direct Items (installed)	
1. Spray-crossflow packed bed scrubbers (3)	285,000
2. Ductwork	16,700
3. Piping	26,200
4. Pumps and motors	41,500
5. Centrifugal fans and motors	33,000
6. Removal of old equipment	12,500
7. Performance test	4,000
Total Direct Items	418,900
B. Indirect Items	
Engineering construction expense, fee, interest on loans during construction, sales tax, freight insurance. (50% of A)	209,500
C. Contingency (25% of A)	104,700
D. Total Capital Investment	733,100
E. Annualized Costs	
1. Cpaital charges	119,500
2. Maintenance	20,000
3. Operating labor	4,000
4. Utilities	21,200
5. Taxes, insurance, administrative	29,400
Total Annualized Costs	194,100

Run-of-Pile Triple Superphosphate

The plant uses the conventional TVA cone process for the production of run-of-pile triple superphosphate. Rated production capacity is approximately 1200 tons of triple superphosphate per day (550 T/D P_2O_5). Actual production averages approximately 800 tons of triple superphosphate per day.

Figure 4-10 provides a flow diagram of the operation. Ground phosphate rock is contacted with phosphoric acid (54 percent P_2O_5) in a TVA cone mixer. The resultant slurry is discharged to the den where solidification of the product occurs. Cutters are used to break up the product before it is sent to storage. A curing period of approximately thirty days is required to allow the reaction to go to completion.

Two initial levels of control will be assumed for the model ROP triple superphosphate plant and retrofit costs estimated for each case. Most actual costs should fall somewhere between the two estimates.

Existing Controls (Case A)

In this case, it is assumed that the plant is in a relatively good state of repair, that necessary ducting and piping changes are moderate, and that the existing ventilation system does not require modification. Replacement of an existing scrubber is assumed to be the major item in the retrofit program.

Gases vented from the cone mixer and the den are currently treated in a 20,000 cfm venturi, combined with the storage building ventilation stream, and sent to a spray tower. The storage building ventilation air is sent directly to the spray tower. This control system has been in operation for approximately five years.

Gypsum pond water serves as the scrubbing liquid for both the venturi and the spray tower. Water is available at 80°F with a fluoride content (as F) of 0.5 weight percent. Additional information regarding the scrubbing liquid is provided in Table 6-7.

Ventilation flow rates and fluoride concentrations for the various sources are listed in Table 6-23. The values listed in this table are estimates based on source test results and control equipment design data. Fluoride removal efficiencies are 86 percent for the venturi treating the combined cone mixer - den gases and 71 percent for the spray tower. Total fluoride emissions from the production and storage facilities are 127 pounds per hour.

Table 6-23. FLOW RATES AND FLUORIDE CONCENTRATIONS FOR ROP-TSP PLANT EMISSION SOURCES[19-21]

Emission Source	Flow Rate (SCFM)	Fluoride Concentration (mg/SCF)	(ppm)
Cone mixer vent gases	500	0.71	30
Curing belt (den) vent gases	24,500	95	4000
Storage building vent gases	125,000	24	1000

Retrofit Controls

The proposed retrofit involves the replacement of the spray tower with a spray-crossflow packed bed scrubber designed for 99 percent fluoride removal. Installation of the new scrubber will reduce fluoride emissions to 4.6 pounds per hour. This emission level is equivalent to the emission guideline of 0.2 pounds fluoride per ton P_2O_5 input.

Moderate rearrangement of the ductwork will be required to install the new scrubber. Existing controls are located as depicted in Figure 6-8. The spray tower will be removed and the spray-crossflow packed bed scrubber installed in the vacated area. A new fan will be required to compensate for the higher pressure drop of the spray-crossflow packed bed scrubber. Existing water lines and pumps will be used to supply gypsum pond water at 40 psig to the spray section. A 16-inch line will be required to supply 2400 gpm of water at 5 psig for the packed bed. Spent scrubbing water is to be recycled to the gypsum pond in the existing drainage system. Treated gases will be emitted from a newly installed 75 foot stack.

Table 6-24 lists the major cost items involved in the retrofit project. Operating conditions for the spray-crossflow packed bed scrubber are presented in Table 6-25. A breakdown of the estimated cost of the project is provided by Table 6-26.

Table 6-24. MAJOR RETROFIT ITEMS FOR MODEL ROP-TSP PLANT (CASE A)

1 Rearrangement of ductwork - removal of spray tower from service and connection of spray-crossflow packed bed scrubber and stack. Requirements are 50 feet of 96-inch* duct.

2. Water line connecting gypsum pond with spray-crossflow packed bed scrubber - 1600 feet of 16-inch pipe.

*Not necessarily circular, but of equivalent cross-sectional area.

3. Two centrifugal pumps (one spare) - 2400 gpm, 76 feet total dynamic head (TDH), 100-horsepower motor.

4. Removal of spray tower.

5. Centrifugal fan - 150,000 SCFM, 355 feet TDH, 200-horsepower motor.

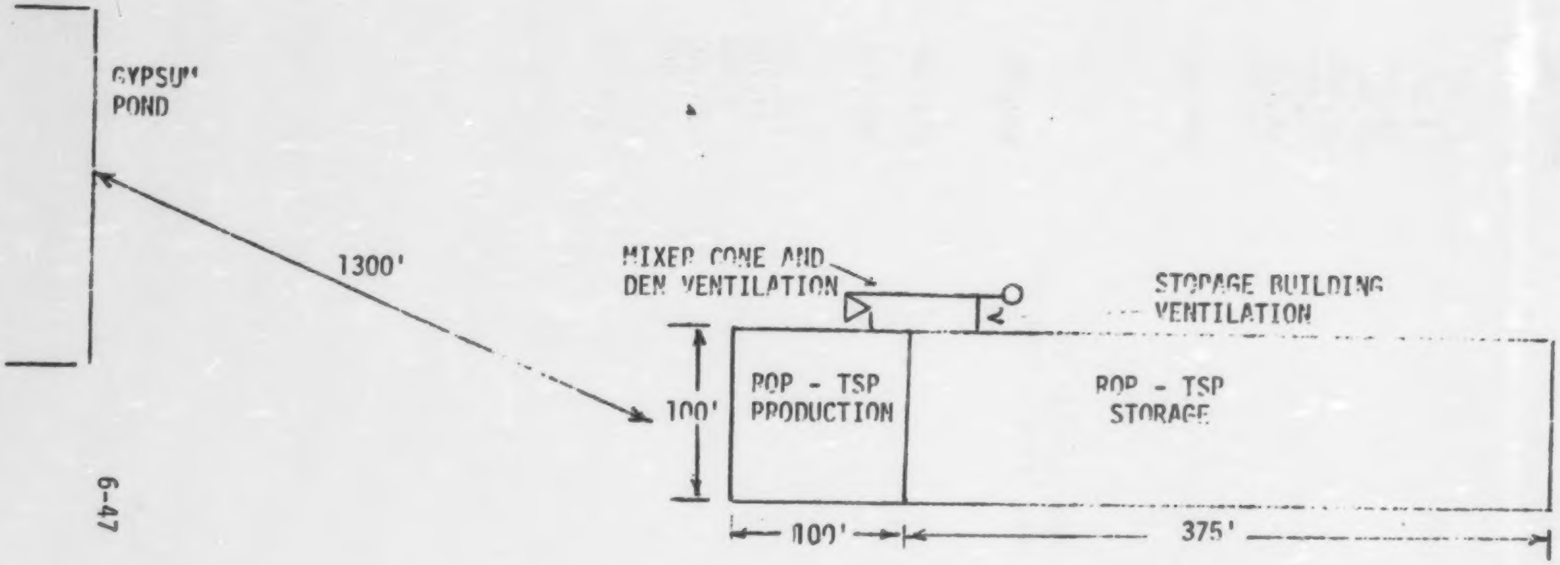
6. Spray-crossflow packed bed scrubber. Unit is designed to handle 158,000 acfm. Using pond water at specified conditions, scrubber must reduce fluoride concentration to 0.23 mg/scf (9.7 ppm) when treating streams listed in Table 6-23.

7. Stack - 75 feet tall, 9 feet diameter.

8. Supports and foundations.

Table 6-25. OPERATING CONDITIONS FOR SPRAY-CROSSFLOW PACKED BED SCRUBBER FOR MODEL POP-TSP PLANT, CASE A (550 Tons/Day P_2O_5)

Gas to scrubber	
Flow, SCFM	150,000
Flow, DSCFM	145,500
Flow, ACFM	158,000
Temp., °F	100
Moisture, Vol. %	3.0
Fluoride (as F), lb/hr	439
Fluoride (as F), ppm	928
Gas from scrubber	
Flow, SCFM	150,000
Flow, DSCFM	145,500
Flow, ACFM	156,000
Temp., °F	90
Moisture, Vol. %	3.0
Fluoride (as F), lb/hr	4.6
Fluoride (as F), ppm	9.7
Fluoride removal, wt %	99.0
Estimated y', ppm	0.8
Estimated NTU required	4.7


GYPSUM
POND
1300'
MIXER CONE AND
DEN VENTILATION
STORAGE BUILDING
VENTILATION
100'
ROP - TSP
PRODUCTION
ROP - TSP
STORAGE
100'
375'

▽ - VENTURI SCRUBBER

○ - SPRAY TOWER SCRUBBER

Figure 6-8. EXISTING CONTROL EQUIPMENT LAYOUT FOR MODEL ROP-TSP PLANT, CASE A

Table 6-26. RETROFIT COSTS FOR MODEL ROP-TSP PLANT, CASE A (550 tons/day P_2O_5) November 1974

	Cost ($)
A. Direct Items (installed)	
1. Spray-crossflow packed bed scrubber	294,000
2. Ductwork	9,800
3. Piping	33,300
4. Pumps and motors	31,900
5. Centrifugal fan and motor	28,800
6. Removal of old equipment	12,500
7. Stack	44,000
8. Performance test	4,000
Total Direct Items	458,300
B. Indirect Items	
Engineering construction expense, fee, interest on loans during construction, sales tax, freight insurance. (50% of A)	229,200
C. Contingency (25% of A)	114,600
D. Total Capital Investment	802,100
E. Annualized Costs	
1. Capital charges	130,700
2. Maintenance	21,700
3. Operating labor	4,000
4. Utilities	26,500
5. Taxes, insurance administrative	32,000
Total Annualized Costs	214,900

Existing Controls (Case B)

In this case, it is assumed that only the production area is originally equipped with controls. A Doyle scrubber is used to treat the combined ventilation streams from the mixing cone and the den. Ventilation flow rates and fluoride concentrations for these sources are presented in Table 6-27. Fluoride removal efficiency of the Doyle scrubber is approximately 69 percent. Emissions from the production area are 95.2 pounds of fluoride per hour with existing controls.

The ROP-TSP storage area is currently uncontrolled. Estimated fluoride emissions from this source are 198 pounds per hour.

Table 6-27. FLOW RATES AND FLUORIDE CONCENTRATIONS OF EFFLUENT STREAMS SENT TO EXISTING CONTROLS.

Emission Source	Flow Rate (SCFM)	Fluoride Concentration (mg/scf)	(ppm)
Cone mixer vent gases	500	0.71	30
Curing belt vent gases	14,500	160	6800

Retrofit Controls (Case B)

The hooding on the curing belt is in a poor state of repair and will be replaced. A new hooding arrangement utilizing a flat stationary air tight top and plastic side curtains will be used. The ventilation rate for the belt will be increased to 24,500 SCFM. This higher flow rate will necessitate the replacement of existing ductwork and fans. The mixing cone will continue to be ventilated at a rate of 500 SCFM.

Control of emissions from the storage area requires the sealing of the building (roof monitor and sides) and the installation of a ventilation system designed to handle 125,000 SCFM. All associated fans, pumps, piping, and ductwork must be installed. The ventilation stream from the storage area will be combined with the effluent stream from the production area and sent to controls. Flow rates and fluoride concentrations associated with the various emission sources are the same as listed in Table 6-23.

Fluoride emissions must be reduced to 4.6 pounds per hour in order to meet the emission guideline of 0.2 pounds fluoride per ton P_2O_5 input. This will be accomplished by removing the Doyle Scrubber and installing a spray-crossflow packed bed scrubber designed for 99.3 percent fluoride removal. Figure 6-9 indicates the placement of the retrofit scrubber. Treated gases will be emitted from a newly installed 75-foot stack.

Gypsum pond water will be used as the scrubbing liquid. Pond water characteristics are listed in Table 6-7. An 18-inch line will be installed to supply the required 3450 gpm of pond water. Spent scrubbing water is to be recycled to the gypsum pond in an existing drainage system.

Table 6-28 identifies the major cost items involved in the retrofit project. Operating conditions for the new scrubber are listed in Table 6-29. Estimated costs are provided in Table 6-30.

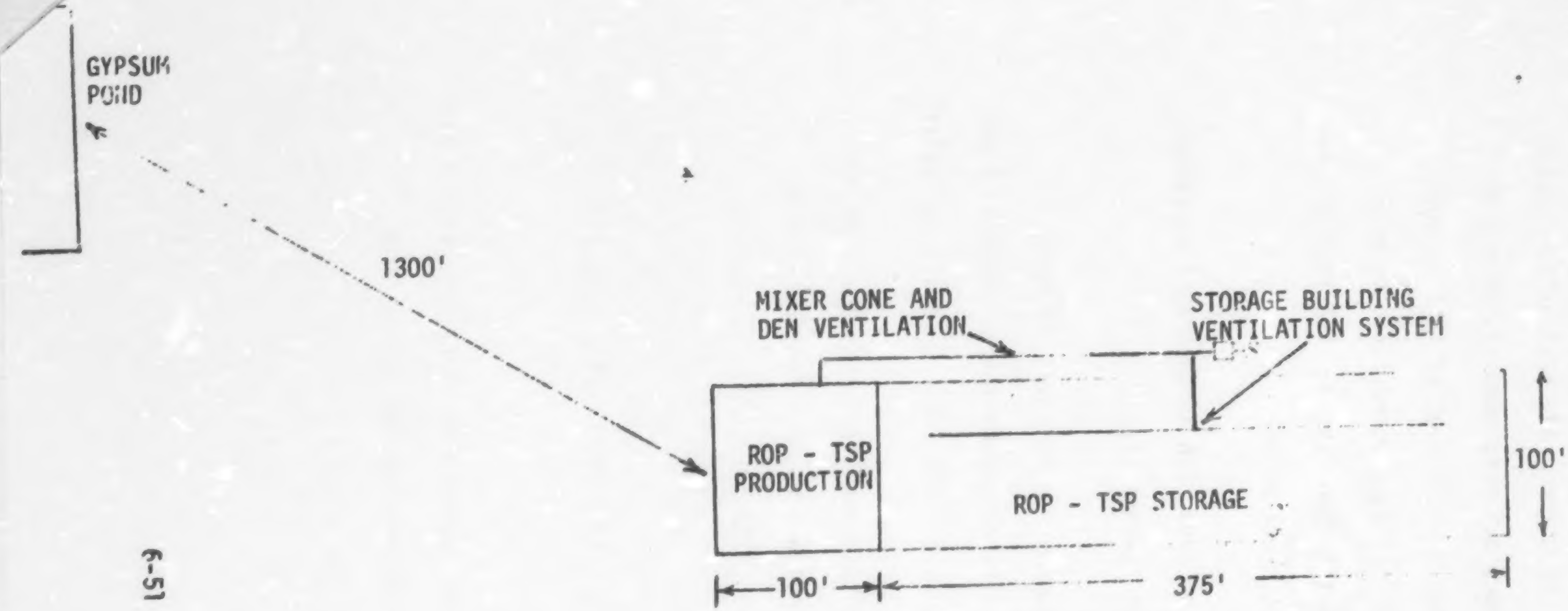

GYPSUM
POND
1300'
MIXER CONE AND
DEN VENTILATION
STORAGE BUILDING
VENTILATION SYSTEM
ROP - TSP
PRODUCTION
ROP - TSP STORAGE
100'
100'
375'

Figure 6-9. RETROFIT CONTROL EQUIPMENT LAYOUT FOR MODEL ROP-TSP PLANT, CASE B

1 - SPRAY CROSSFLOW PACKED BED SCRUBBER

2 - STACK

Table 6-28. MAJOR RETROFIT ITEMS FOR MODEL ROP-TSP PLANT (CASE B)

1. Ductwork - replacement of the curing belt ventilation system and installation of a storage building ventilation system. Curing belt ventilation system - 175 feet of 42-inch duct with a 50 foot branch of 6-inch duct connecting the mixing cone. Storage building ventilation system - 150 feet of 96-inch duct with two 160-foot branches of 66-inch duct.

2. Water line connecting gypsum pond with spray-crossflow packed bed scrubber - 1700 feet of 18-inch pipe.

3. Two centrifugal pumps (one spare) - 3450 gpm, 74 feet total dynamic head (TDH), 125-horsepower motor. Booster pump for spray section - 1150 gpm, 81-feet TDH, 40-horsepower motor.

4. Centrifugal fan for curing belt ventilation system - 25,000 SCFM, 760 feet TDH, 75-horsepower motor. Fan for storage building ventilation system - 125,000 SCFM, 725 feet TDH, 350 horsepower motor.

5. Removal of - 1) old hooding system from curing belt and 2) Doyle scrubber.

6. Installation of a new hooding system consisting of a wooden air-tight top and plastic side curtains on the curing belt.

7. Sealing of the storage building - roof monitor and sides of building.

8. Spray-crossflow packed bed scrubber. Unit is designed to handle 158,000 acfm. Using pond water at specified conditions, scrubber must reduce fluoride concentration to 0.23 mg/scf (9.7 ppm) when treating streams listed in Table 6-23.

9. Stack - 75 feet tall, 9 foot diameter.

10. Supports and foundations.

Table 6-29. OPERATING CONDITIONS FOR SPRAY-CROSSFLOW PACKED BED SCRUBBER FOR MODEL ROP-TSP PLANT, CASE B
(550 Tons/Day P_2O_5)

Gas to Scrubber	
Flow, SCFM	150,000
Flow, DSCFM	145,500
Flow, ACFM	158,000
Temp., °F	100
Moisture, Vol. %	3.0
Fluoride (as F), lb/hr	703
Fluoride (as F), ppm	1490
Gas from Scrubber	
Flow, SCFM	150,000
Flow, DSCFM	145,500
Flow, ACFM	156,000
Temp., °F	90
Moisture, Vol. %	3.0
Fluoride (as F), lb/hr	4.6
Fluoride (as F), ppm	9.7
Fluoride removal, wt %	99.3
Estimated y', ppm	0.8
Estimated NTU required	5.1

Table 6-30. RETROFIT COSTS FOR MODEL ROP-TSP PLANT, CASE B*
(550 tons/day P_2O_5) November 1974

		Cost ($)
A.	Direct Items (installed)	
	1. Spray-crossflow packed bed scrubber	294,000
	2. Ductwork	89,200
	3. Piping	39,800
	4. Pumps and motors	48,200
	5. Centrifugal fans and motors	40,800
	6. Curing belt hooding	26,700
	7. Sealing of storage building	80,000
	8. Removal of old equipment	20,000
	9. Stack	44,000
	10. Performance test	4,000
	11. Structural steel supports/bldg.	100,000
	Total Direct Items	786,700
B.	Indirect Items Engineering construction expense, fee, interest on loans during construction, sales tax, freight insurance. (50% of A)	393,400
C.	Contingency (25% of A)	196,700
D.	Total Capital Investment	1,376,800
E.	Annualized Costs	
	1. Capital charges	224,400
	2. Maintenance	37,100
	3. Operating labor	4,000
	4. Utilities	48,200
	5. Taxes, insurance, administrative	55,700
	Total Annualized Costs	369,400

*In costing this model, extensive use was made of a project report dated June 27, 1974, prepared by Jacobs Engineering company for J. R. Simplot Co., Pocatello, Idaho.

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Granular Triple Superphosphate Production and Storage

The model plant uses the Dorr-Oliver process for the production of granular triple superphosphate. Designed production capacity is 870 tons of triple superphosphate per day (400 T/D P_2O_5). Figure 4-13 provides a schematic diagram of the operation.

Ground phosphate rock and phosphoric acid (39 percent P_2O_5) are contacted in a series of reactors. The reaction mixture is then pumped to the granulator where it is mixed with recycled material from the cyclone dust collectors and the screening operations to produce product sized granules of triple superphosphate. A rotary drier is used to reduce the product moisture content to about 3 percent.

Dried triple superphosphate is cooled and screened before being sent to storage. A curing period of 3 to 5 days is provided before the product is considered ready for shipping. Shipping of GTSP is on a seasonal basis, therefore, a large storage capacity is required. The storage facility has a capacity of 25,000 tons of a triple superphosphate (11,500 tons P_2O_5). This building is ventilated at a rate of 75,000 scfm using a roof monitor.

Existing Controls

Gases vented from the reactors and the granulator are combined and treated in a two-stage system consisting of a venturi and a cyclonic spray tower. Gypsum pond water serves as the scrubbing liquid in both units. Pond water is available at 80°F with a fluoride content of 0.5 percent. Additional properties are listed in Table 6-7. . Fluoride removal efficiency is 85 percent for the venturi scrubber and 82 percent for the cyclonic spray tower.

The drier gases are passed through cyclones for product recovery and then treated for fluoride removal by a two-stage scrubbing system (venturi-cyclonic spray tower) similar to that described for the reactor-granulator cases. Fluoride collection is 85 percent in the venturi and 86 percent in the cyclonic scrubber. Gypsum pond water is used as the scrubbing liquid.

Miscellaneous gas streams vented from the product cooling and screening operations are a third source of emissions from the GTSP production facility. These streams are combined and treated for product recovery (dry cyclone) and fluoride removal (cyclonic spray tower). Fluoride collection efficiency of the cyclonic spray tower is 87 percent.

Existing controls have been in operation for five years. Flow rates and fluoride concentrations for the various emission sources are listed in Table 6-31. All values are estimates based on a combination of source test results and published data. Total fluoride emissions from the production facilities are 31.0 pounds per hour.

Ventilation air from the storage building is presently emitted uncontrolled. Table 6-31 lists the estimated volumetric flow rate and fluoride concentration based on source test data. Fluoride emissions from the storage building are 13.2 pounds per hour.

Table 6-31. FLOW RATES AND FLUORIDE CONCENTRATIONS FOR GTSP PLANT EMISSION SOURCES[22-24]

Emission source	Flow rate (SCFM)	Fluoride concentration (mg/SCF)	(ppm)
Reactor-granulator gases	18,000	84	3500
Drier vent gases	48,000	84	3500
Cooler & screening equipment gases	51,000	16.8	700
Storage building ventilation	75,000	1.3	54

Retrofit Controls

The retrofit project for the GTSP production facility involves the replacement of the cyclonic spray tower on the reactor-granulator stream and on the drier stream with a spray-crossflow packed bed scrubber. A third spray-crossflow packed bed unit will be installed on the miscellaneous stream to provide secondary scrubbing. The new control system is designed to reduce fluoride emissions from the production operation to 3.34 pounds per hour. This emission rate is equivalent to the emission guideline of 0.2 pounds fluoride per ton P_2O_5 input.

Figure 6-10 shows the position of existing controls. Retrofit plans call for the removal of the cyclonic spray towers treating the reactor-granulator and the drier gases and the installation of spray-crossflow packed bed scrubbers in the vacated areas. The spray-crossflow packed bed scrubber for the miscellaneous stream will also be located adjacent to the preliminary scrubber as indicated in Figure 6-11.

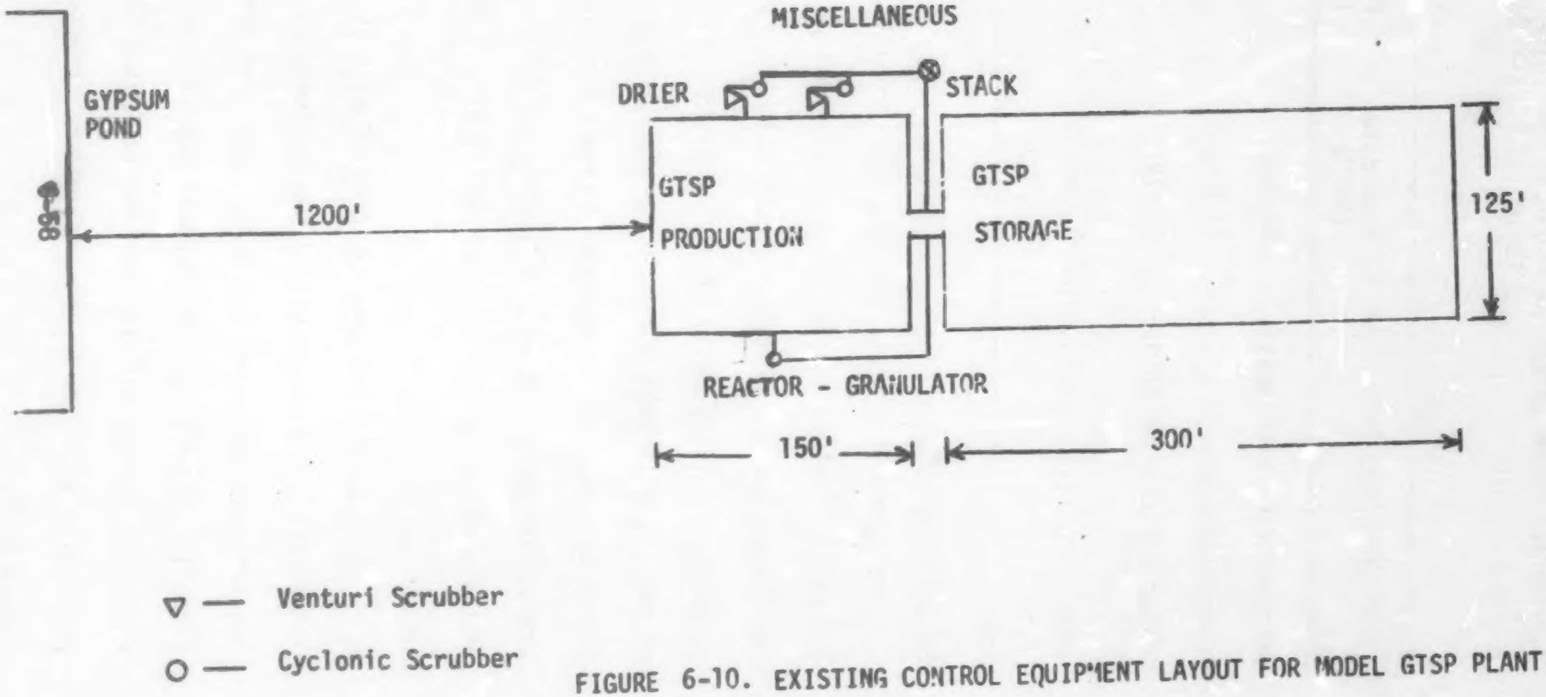
MISCELLANEOUS
DRIER
STACK
GYPSUM POND
GTSP PRODUCTION
GTSP STORAGE
1200'
125'
REACTOR - GRANULATOR
150'
300'
▽ — Venturi Scrubber
○ — Cyclonic Scrubber

FIGURE 6-10. EXISTING CONTROL EQUIPMENT LAYOUT FOR MODEL GTSP PLANT.

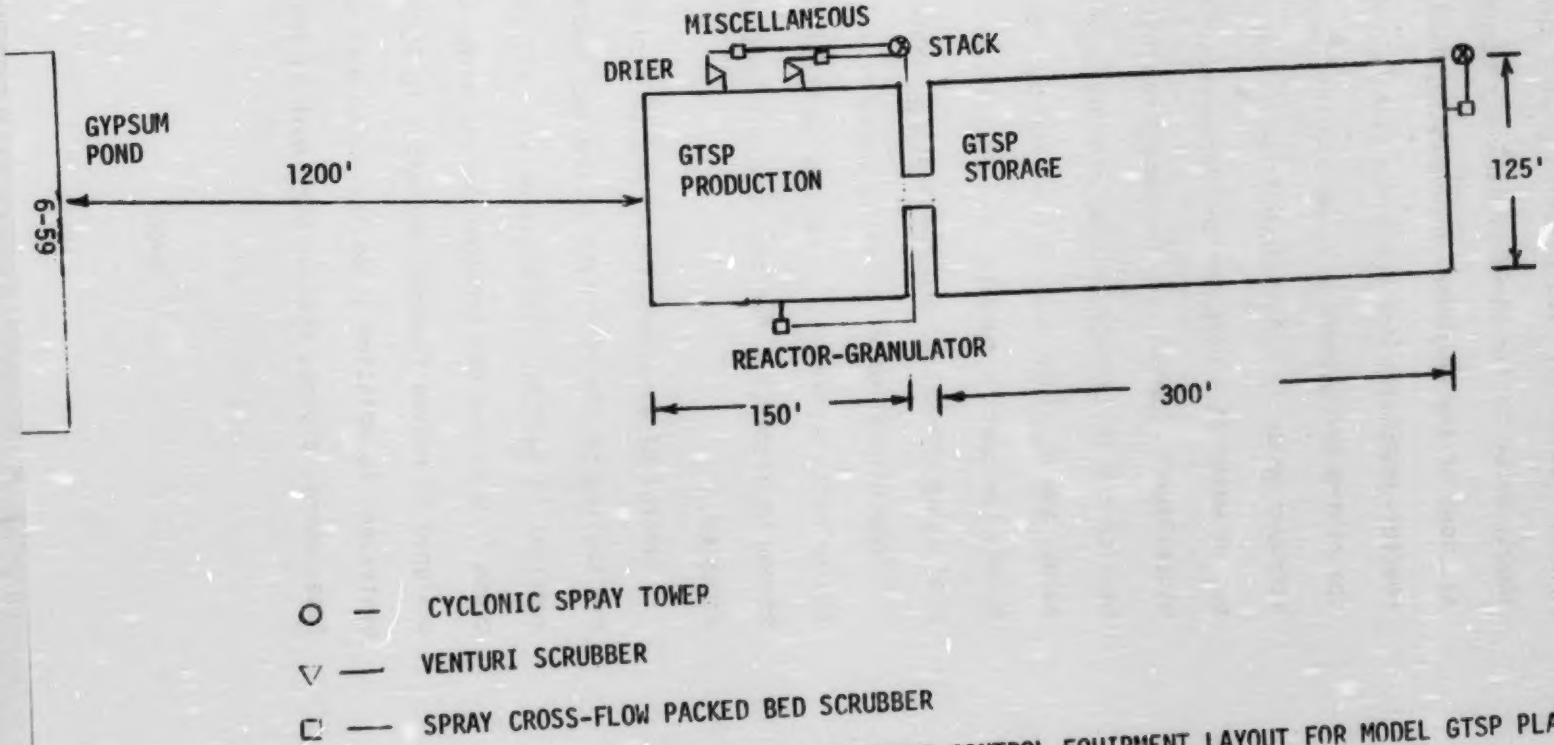
MISCELLANEOUS
DRIER
STACK
GYPSUM POND
1200'
GTSP PRODUCTION
GTSP STORAGE
125'
REACTOR-GRANULATOR
150'
300'
○ — CYCLONIC SPPAY TOWEP
▽ — VENTURI SCRUBBER
☐ — SPRAY CROSS-FLOW PACKED BED SCRUBBER

FIGURE 6-11. RETROFIT CONTROL EQUIPMENT LAYOUT FOR MODEL GTSP PLANT.

Existing pumps, fans, piping and ductwork will be utilized wherever possible. The existing piping system will be used to supply water to the three preliminary scrubbers and the spray sections of the secondary (spray-crossflow packed) scrubbers on the reactor-granulator and the drier streams. Some minor alteration in the piping arrangement will be required because of changes in the scrubber geometry. A 16-inch line will be installed to provide 2160 gpm of water at 5 psig for the spray-crossflow packed bed unit on the miscellaneous stream and the packed sections of the secondary scrubbers on the reactor-granulator and the drier streams. Duplicate pumps, one on stand-by, will be provided for this service. In all cases, the spent scrubbing liquid will be recycled to the gypsum pond using the existing plant drainage system.

Some alteration of existing ductwork will be required to install the retrofit scrubbers. A new fan will be installed on the miscellaneous stream to compensate for the pressure loss caused by the secondary scrubber.

Control of emissions from the GTSP storage facility requires the sealing of the roof monitor and the installation of 350 feet of ventilation ducting. Ventilation air will be treated in a spray-cross flow packed bed scrubber before being emitted. The unit is designed to reduce fluoride emissions to 1.25 pounds per hour; a rate equivalent to emission guideline under most conditions. All associated fans, pumps, piping, and ductwork must be installed. The existing plant drainage system will be used to recycle gypsum pond water. Figure 6-11 provides a view of the equipment layout.

All major retrofit items are tabulated in Table 6-32. Table 6-33 provides a list of operating conditions for the four retrofitted spray-crossflow packed bed scrubbers. Table 6-34 presents the retrofit project costs.

Table 6-32. MAJOR RETROFIT ITEMS FOR MODEL GTSP PLANT

GTSP Production

1. Rearrangement of ductwork - removal of existing cyclonic scrubbers on reactor-granulator and drier streams and connection of replacement spray-crossflow packed bed scrubbers. Installation of third spray-crossflow packed bed unit on miscellaneous stream. Requirements are 150 feet of 60-inch diameter duct and 50 feet of 42-inch duct.

2. New water line connecting gypsum pond with retrofitted scrubbers - 1200 feet of 16-inch pipe with 200-foot branch of 14-inch pipe to scrubbers treating the drier and miscellaneous streams and 150 foot branch of 5-inch pipe to the reactor-granulator scrubber.

3. Two centrifugal pumps, each 2160 gpm, 105 feet total dynamic head (TDH), 100-horsepower motor. Booster pump for spray section of spray-crossflow packed bed scrubber on miscellaneous stream - 374 gpm, 89 feet TDH, 10-horsepower motor.

Table 6-32. MAJOR RETROFIT ITEMS FOR MODEL GTSP PLANT (cont.)

4. Centrifugal fan for miscellaneous stream - 51,000 scfm, 356 feet TDH, 75-horsepower motor.

5. Removal of cyclonic scrubbers on reactor-granulator and miscellaneous streams.

6. Three spray-crossflow packed bed scrubbers. Design parameters are provided in Table 6-33. Using pond water at specified conditions, the scrubbers are required to meet the indicated emission levels when treating the gases described in Table 6-31.

7. Supports and foundations.

GTSP Storage

1. Sealing of roof monitor and installation of ducting - 350 feet of 78-inch ducting for ventilation of building and connection of scrubber.

2. Water line connecting gypsum pond with spray-crossflow packed bed scrubber - 1700 feet of 12-inch pipe.

3. Centrifugal pump - 1730 gpm, 81 feet TDH, 60-horsepower motor. Booster pump for spray section - 580 gpm, 89 feet TDH, 15-horsepower motor.

4. Centrifugal fan - 75,000 scfm, 630 feet TDH, 200 horsepower motor.

Table 6-32. MAJOR RETROFIT ITEMS FOR MODEL GTSP PLANT (cont).

5. Spray-crossflow packed bed scrubber. Using specified pond water, scrubber must reduce fluoride concentration of ventilation stream to 0.13 mg/scf (5.1) when treating the gases described in Table 6-31.

6. Supports and foundations.

7. Stack - 50 feet tall, 6 foot diameter.

Table 6-33. OPERATING CONDITIONS FOR SPRAY-CROSSFLOW PACKED BED SCRUBBERS FOR MODEL GTSP PLANT

(400 Tons/Day P_2O_5)

	Production			Storage
	Reactor	Drier	Cooler	Ventilation
Gas to Scrubber				
Flow, SCFM	18,000	48,000	51,000	75,000
Flow, DSCFM	16,560	44,160	48,450	74,480
Flow, ACFM	19,400	52,500	54,900	77,100
Temp., °F	110	120	110	87
Moisture, vol. %	8.0	8.0	5.0	0.7
Fluoride (as F), lb/hr	28	79.8	14.8	13.2
Fluoride (as F), ppm	490	525	92	54.1
Gas from Scrubber				
Flow, SCFM	16,850	45,050	49,400	76,000
Flow, DSCFM	16,560	44,160	48,450	74,480
Flow, ACFM	17,500	46,800	51,200	78,100
Temp., °F	90	90	90	85
Moisture, vol. %	2.0	2.0	2.0	2.0
Fluoride (as F), lb/hr	1.00	1.76	0.63	1.25
Fluoride (as F), ppm	17.5	11.5	3.9	5.1
Fluoride removal, wt %	96.5	97.8	96.0	90.5
Estimated y', ppm	0.95	0.95	0.85	0.7
Estimated NTU required	3.38	3.90	3.39	2.49

Table 6-34. RETROFIT COSTS FOR MODEL
GTSP PLANT (400 tons/day P_2O_5) November 1974

	Cost ($)
A. Direct Items (installed)	
1. GTSP Production	
a. Spray-crossflow packed bed scrubbers (3)	261,000
b. Ductwork	22,800
c. Piping	26,200
d. Pumps and motors	35,900
e. Removal of old equipment	18,000
f. Performance test	4,000
g. Centrifugal fan and motor	14,400
2. GTSP Storage	
a. Cross flow packed scrubber	150,000
b. Ductwork	56,600
c. Piping	27,800
d. Pumps and motors	19,400
e. Centrifugal fan and motor	23,000
f. Structural steel supports/bldg.	50,000
g. Sealing of storage building	10,000
h. Performance test	4,000
Total Direct Items	723,100
B. Indirect Items	
Engineering construction expense, fee, interest on loans during construction, sales tax, freight insurance. (50% of A)	361,600
C. Contingency (25% of A)	180,800
D. Total Capital Investment	1,265,500
E. Annualized Costs	
1. Capital charges	206,300
2. Maintenance	33,800
3. Operating labor	6,000
4. Utilities	40,600
5. Taxes, insurance, administrative	50,500
Total Annualized Costs	337,200

6.1.3.2 Retrofit Case Descriptions

General Procedure

This section describes two actual cases in which control systems containing spray-crossflow packed bed scrubbers were added to existing production facilities. Each case description provides the following information:

1. A description of the process in use,
2. Identification of the original fluoride controls and sources treated,
3. A description of the retrofit project, and
4. Retrofit costs.

Case A

Case A involves the retrofitting of controls to a granular triple superphosphate plant. This facility was built in 1953 using the Dorr-Oliver slurry granulation process. Annual production capacity was originally 100,000 tons triple superphosphate but improvements in plant design have almost doubled this value.

The production equipment is housed in a structure which also contains a second granular triple superphosphate plant and a run-of-pile triple superphosphate plant. All available space within the building is in use and any rearrangement of equipment or ducting would require major modifications. Space limitations also exist in the area immediately surrounding the building and would affect any retrofit project.

Original Controls

Fluoride control was initially provided by a spray tower installed in 1953 as part of the original plant design. Gypsum pond water was used as the scrubbing liquid. Ventilation streams from the drier and the product screens were sent to the spray tower while both reactor and granulator gases were vented directly to the atmosphere. The spray tower was improved in 1964 by the addition of more sprays and a mist elimination section. Performance data for this system is not available.

Retrofit Controls

The spray tower was removed in 1966 as part of a retrofit project and replaced by a three stage scrubbing system. Gases vented from the drier (60,000 acfm) and the screens (40,000 acfm) are now treated in separate venturi scrubbers, combined, passed through a cyclonic scrubber, and finally treated in a spray-crossflow packed bed scrubber. Operating characteristics of these units are listed in Table 6-35. Pond water serves as the scrubbing liquid for the entire system. Controls for the reactor and the granulator were not added at this time.

All associated fans, pumps, piping, ductwork, and stacks were installed as part of the retrofit project. New pond water supply and drainage systems were also required.

Designed fluoride removal efficiency is 99+ percent. Tests conducted by the Environmental Protection Agency in June 1972 measured fluoride removal efficiencies ranging up to 99.6 percent.

Table 6-35. OPERATING CHARACTERISTICS OF SCRUBRERS IN RETROFIT CASE A

Scrubber type	Scrubbing liquid to gas ratio (gal/SCF)	Gas stream pressure drop(in. H_2O
Drier venturi	0.008	12-15
Screen venturi	0.006	8-13
Cyclonic scrubber	0.007	4-6
Spray-crossflow packed bed scrubber	0.002	2-6

Retrofit Costs

Total installed cost of the retrofit control equipment was $368,000, however, this does not include the cost of removing old equipment or of adding new pond water supply and drainage systems. The annual operating cost is reported to be $51,000.

Case B

Case B is similar to Case A in most respects. The facility involved is a granular triple superphosphate plant built in 1953. This plant also uses the Dorr-Oliver process for GTSP. Annual capacity is approximately 200,000 tons triple superphosphate. Space limitations are similar to those described in Case A.

Original Controls

Emissions from the drier and the screening area were controlled by a spray tower which had been installed as part of the original plant design. Fluoride removal efficiency data is not available for this system. Reactor and granulator gases were vented to the atmosphere without treatment.

Retrofit Controls

The retrofit project consisted of the removal of the spray tower and its replacement by a system similar to that described in Case A. Controls are in three stages - 3 venturis in parallel followed by a cyclonic scrubber and a spray-crossflow packed bed scrubber. Effluent streams from the drier and the screens are treated in separate venturis, combined with the gases from the third venturi, and sent to the remaining controls. The third venturi treats gases from either an adjacent wet acid plant or a nearby run-of-pile triple superphosphate plant. Designed capacity of the control system is 115,000 acfm. Gypsum pond water serves as the scrubbing liquid. Controls for the reactor and the granulator were not installed as a part of this project.

The retrofit controls were added in 1972. All associated fans, pumps, piping, and ducting were installed as part of this project. Fluoride removal efficiency of the system is reported to be 99+ percent.

Retrofit Costs

Total installed cost for the retrofit controls was reported to be $760,000. Table 6-36 lists a breakdown of the cost. Demolition costs and the cost of adding new pond water supply and drainage systems are not included. No operating costs were provided.

Table 6-36. CASE B RETROFIT PROJECT COSTS

Item	Installed Cost (dollars)
Foundations	81,000
Structural steel	52,000
Blowers and motors	85,000
Wet scrubbers	218,000
Pumps, sumps and piping	175,000
Ducts and stack	102,000
Electrical and instruments	47,000

6.2 VENTURI SCRUBBER

6.2.1 Description

Venturi scrubbers are primarily particulate collection devices, however, they are also applicable to gas absorption work and are in widespread use throughout the phosphate fertilizer industry. They are particularly well suited for treating effluent streams containing large amounts of solids or silicon tetrafluoride because of their high solids handling capacity and self-cleaning characteristics. Operational reliability and low maintenance requirements are major reasons for the popularity of this scrubber design.

A venturi provides a high degree of gas-liquid mixing but the relatively short contact time and the cocurrent flow of the scrubbing liquid tend to limit its absorption capabilities. When treating effluent streams requiring a high degree of fluoride removal, venturis are often used as the initial component in a multiple-scrubber system.

Two types of venturi scrubbers, gas actuated and water actuated, are in general use. In both cases, the necessary gas-liquid contacting is obtained from velocity differences between the two phases and turbulence in the venturi throat. Both types also require the use of a mist elimination section for removal of entrained scrubbing liquid. The major difference between the designs is the source of motive power for operating the scrubber. In the case of the gas actuated venturi, the velocity of the gas stream provides the energy required for gas-liquid contacting. The scrubbing liquid is introduced into the gas stream at the throat of the venturi and is broken into fine droplets by the accelerating gas stream. Pressure drop across the scrubber is generally high - from 8 to 20 inches of water. A fan is required to compensate for this loss in gas stream pressure. Figure 6-12 provides a schematic diagram of a gas actuated venturi.

A water acutated venturi is pictured in Figure 6-13. In this case, the scrubbing liquid is introduced at a high velocity through a nozzle located upstream of the venturi throat. The velocity of the water streams is used to pump the effluent gases through the venturi. Drafts of up to 8 inches of water can be developed at high liquid flow rates.[25]

The removal of the fan from the system makes the water actuated venturi mechanically simpler, more reliable, and less costly than the gas actuated type. An additional advantage is its relative insensitivity to variations in the gas stream flow rate.[26] Gas actuated venturis rely upon the gas stream velocity for the energy for gas-liquid contacting, therefore, variations in the gas flow can greatly affect scrubber efficiency. The performance of the water-actuated venturi depends mainly on the liquid stream velocity.

Water actuated venturis find application principally as gas absorption units.[25] Their use is usually limited, however, to small gas streams with moderate scrubbing requirements. The water-actuated venturi is seldom used for gas flows greater than 5,000 acfm because of the large water requirements.[26]

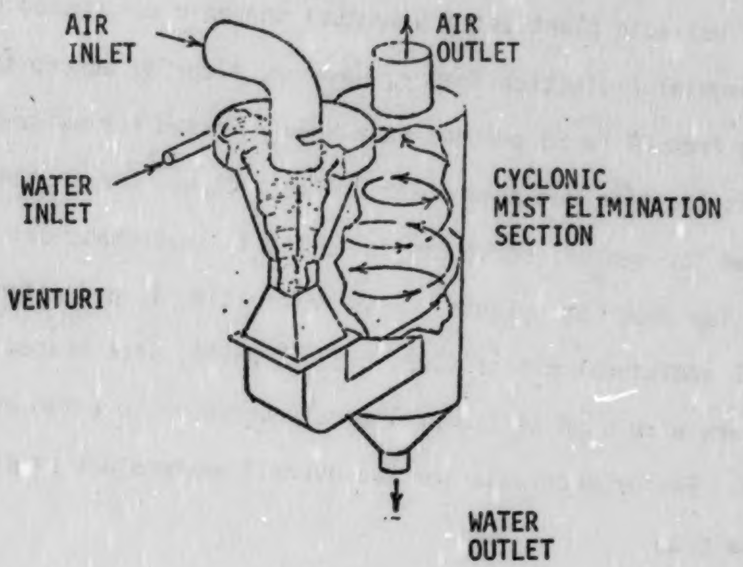
AIR INLET
AIR OUTLET
WATER INLET
CYCLONIC MIST ELIMINATION SECTION
VENTURI
WATER OUTLET

FIGURE 6-12. GAS ACTUATED VENTURI SCRUBBER WITH CYCLONIC MIST ELIMINATOR.

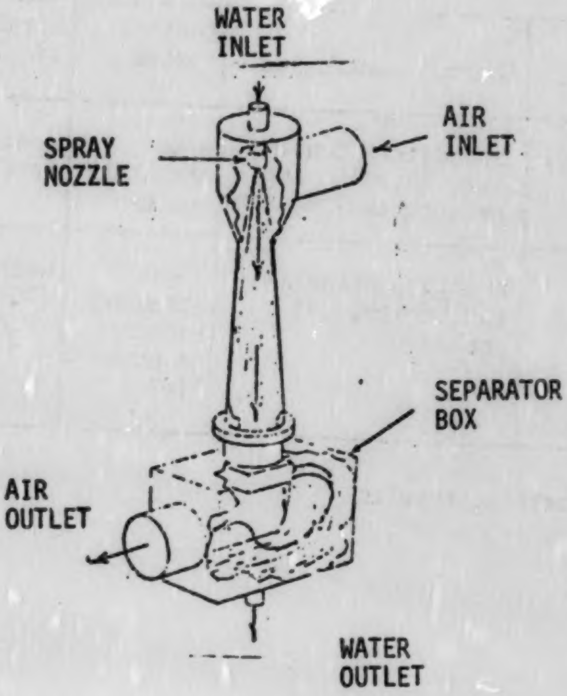
WATER INLET
AIR INLET
SPRAY NOZZLE
SEPARATOR BOX
AIR OUTLET
WATER OUTLET

FIGURE 6-13. WATER ACTUATED VENTURI.

6.2.2 Emission Reduction

No wet-acid plant using a venturi scrubber was tested by the Environmental Protection Agency, however, fluoride absorption efficiency ranging from 84 to 96 percent have been reported for water-actuated venturis treating wet-acid plant effluent gases.[27] Performance data was obtained for venturi scrubbers installed in superphosphoric acid and diammonium phosphate plants. This information is presented in Table 6-37. Several additional plants (DAP, GTSP, ROP-TSP) were tested at which venturi scrubbers were used as the preliminary scrubber in a two or three stage system. Performance data for the overall systems are presented in Tables 6-3 and 6-40.

Table 6-37. VENTURI SCRUBBER PERFORMANCE IN SUPERPHOSPHORIC ACID AND DIAMMONIUM PHOSPHATE PLANTS[28]

Type of plant	Sources controlled	Control system	Scrubbing liquid	Fluoride emissions[a] (lb F/ton P_2O_5)
Vacuum evaporation SPA	barometric condenser, hotwell, and product cooling tank	water actuated venturi	pond water	0.0009
DAP	reactor, granulator, drier, and cooler	3 gas actuated venturis in parallel	weak acid (20-22% P_2O_5)	0.129

[a] Average of testing results

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6.2.3 Retrofit Costs for Venturi Scrubbers

This section evaluates the costs involved with retrofitting venturi scrubbers in a diammonium phosphate plant. Venturis might be used to provide fluoride control for this source because of their high solids handling capability. Only the retrofit model approach will be used to provide costs.

The model plant is the same as described in section 6.1.3.1. To avoid repetition, only a summary of retrofit controls, a list of major retrofit items, and a breakdown of costs will be presented here.

The general aspects of the retrofit project are the same as described in Section 6.1.3.1. Gas-actuated venturis will be used as fluoride scrubbers on the reactor-granulator, the drier, and the cooler streams. Pumping and fan requirements differ from those presented in section 6.1.3.1. An existing line will be used to supply part of the water requirement. Table 6-38 provides a list of major retrofit items required. Costs are presented in Table 6-39.

Table 6-38. MAJOR RETROFIT ITEMS FOR MODEL DAP PLANT

1. Ductwork - removal of cyclonic spray tower from service and connection of three gas-actuated venturi scrubbers. Requirements are 100 feet of 60-inch duct and 50 feet of 54-inch duct.

2. Water line connecting gypsum pond with venturi scrubbers - 1200 feet of 16-inch pipe with 200-foot branch of 14-inch

pipe and 150-foot branch of 6-inch pipe.

3. Two centrifugal pumps (one spare) - 2550 gpm, 195 feet total dynamic head (TDH), 150 horsepower motor.

4. Three centrifugal fans: one for the reactor-granulator stream, one for the drier stream, and one for the cooler stream. Reactor-granulator fan - 30,000 scfm, 713 feet TDH, 75 horsepower motor. Drier stream fan and cooler stream fan - 45,000 scfm, 713 feet TDH, 125 horsepower motor.

5. Removal of cyclonic spray tower.

6. Three venturi scrubbers equipped with mist eliminator sections. When using specified pond water and treating gases described in Table 6-19, scrubbers are required to obtain performance indicated in Table 6-21.

7. Supports and foundations.

Table 6-39. RETROFIT COSTS FOR MODEL DAP PLANT (500 Tons/Day P_2O_5) November 1974

	Cost ($)
A. Direct Items (installed)	
1. Venturi scrubbers (3)	181,700
2. Ductwork	17,000
3. Piping	26,500
4. Pumps and motors	39,200
5. Centrifugal fans and motors	38,400
6. Removal of old equipment	12,500
7. Performance test	4,000
Total Direct Items	319,300
B. Indirect Items Engineering construction expense, fee, interest on loans during construction, sales tax, freight insurance (50% of A.)	159,700
C. Contingency (25% of A.)	79,800
D. Total Capital Investment	558,800
E. Annualized Costs	
1. Capital charges	91,100
2. Maintenance	15,000
3. Operating labor	4,000
4. Utilities	31,000
5. Taxes, insurance, administrative	22,400
Total Annualized Costs	163,500

6.3 SPRAY TOWER SCRUBBER

6.3.1 Description

Spray towers provide the interphase contacting necessary for gas absorption by dispersing the scrubbing liquid in the gas phase in the form of a fine spray. Several types of spray towers are in general use. The simplest consists of an empty tower equipped with liquid sprays at the top and a gas inlet at the bottom. Scrubbing liquid is sprayed into the gas stream and droplets fall by gravity through a upward flow of gas. This design has the advantages of a very low pressure drop and an inexpensive construction cost but it can provide only about one transfer unit for absorption.[29] Entrainment of scrubbing liquid is also a problem.

Cyclonic spray towers eliminate the excessive entrainment of scrubbing liquid by utilizing centrifugal force to remove entrained droplets. Figure 6-14 is a schematic diagram of a typical design. In this case, a tangential inlet is used to impart the spinning motion to the gas stream. Water sprays are directed parallel to the gas flow providing crossflow contacting of the gas and liquid streams. Pressure drops across the scrubber ranges from 2 to 8 inches of water. Solids handling capacity is high, however, absorption capacity is limited to about two transfer units.[29,30]

6.3.2 Emission Reduction

Fluoride removal efficiencies ranging from 84 to 95 percent have been reported for cyclonic spray towers treating wet acid plant

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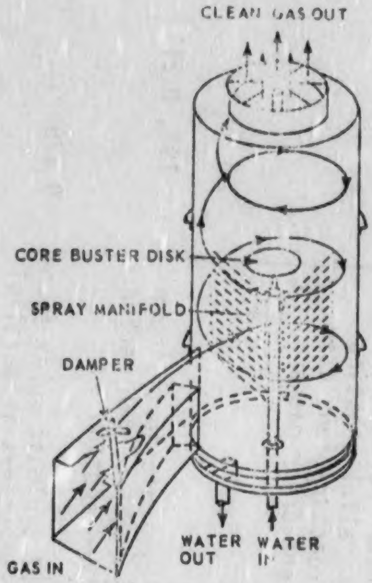


FIGURE 6-14. CYCLONIC SPRAY TOWER SCRUBBER.

effluent gases.[31] Table 6-40 presents performance data obtained by the Environmental Protection Agency for cyclonic spray towers installed in wet-process phosphoric acid, diammonium phosphate, and run-of-pile triple superphosphate plants. In most cases, the control system consisted of a primary venturi scrubber or cyclonic spray tower followed by a secondary cyclonic spray tower. Gypsum pond water was used as the scrubbing solution except where indicated.

6.3.3 Retrofit Costs for Cyclonic Spray Towers

This section will use the retrofit model approach to estimate the costs involved with the installation of cyclonic spray towers in a DAP-TSP plant. Control systems utilizing cyclonic spray towers are capable of providing the collection efficiency necessary to meet the emission guideline of 0.2 pounds fluoride per ton P_2O_5 input.

Table 6-40. CYCLONIC SPRAY TOWER PERFORMANCE IN WET-PROCESS PHOSPHORIC ACID, DIAMMONIUM PHOSPHATE, AND RUN-OF-PILE TRIPLE SUPERPHOSHATE PLANTS [32]

Type of plant	Sources controlled	Primary controls	Secondary controls	Fluoride emissions[a] (lb F/ton P_2O_5)
WPPA	reactor, filter, and miscellaneous sources	two-stage cyclonic spray tower	—	0.056
DAP	reactor, granulator, drier, and cooler	3 cyclonic spray tower scrubbers in parallel. Scrubbers treating reactor-granular and drier gases use weak (28-30% P_2O_5) acid	2 cyclonic spray tower scrubbers in parallel treating reactor-granulator and drier gases	0.380
ROP-TSP	mixing cone, den, transfer conveyor, and storage pile	venturi scrubber	cyclonic spray tower scrubber with packed bed section	0.194, 0.211[b]
ROP-TSP	mixing cone, den, and storage pile	2 cyclonic spray tower scrubbers in parallel	2 cyclonic spray tower scrubbers in parallel	0.125

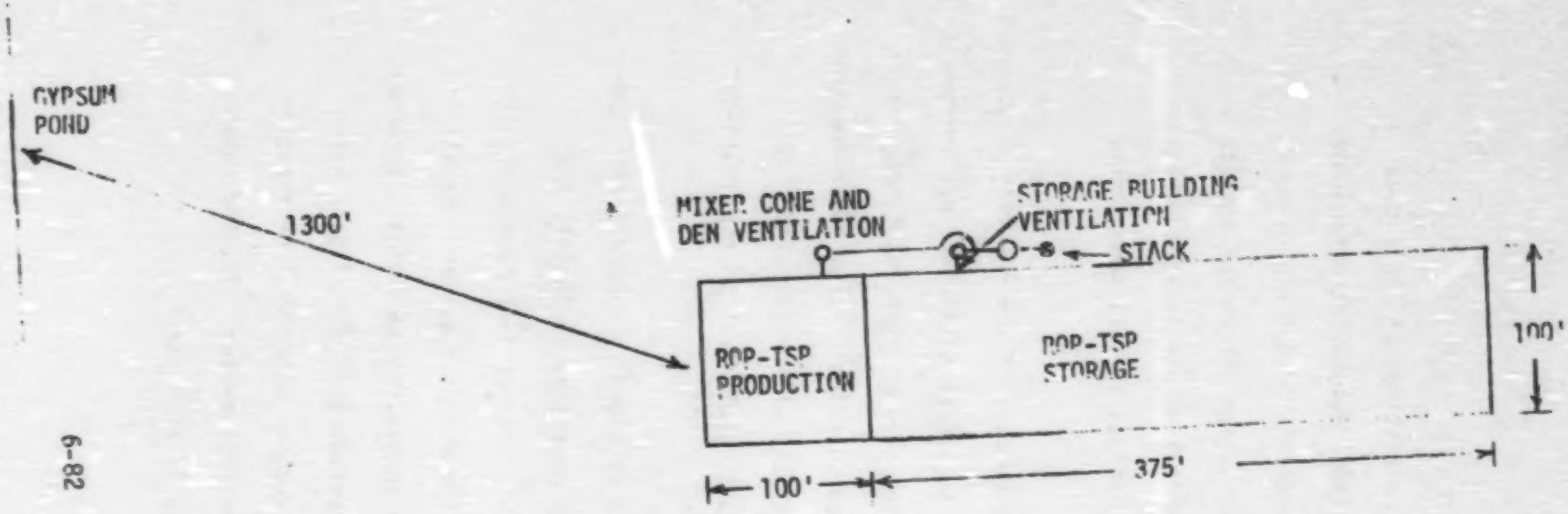
[a] Average of testing results

[b] Second series of tests

The model plant is the same as described in section 6.1.2.1 (Case A). Flow rates and fluoride concentrations of the various effluent streams are listed in Table 6-23. Gases vented from the cone mixer and den are presently treated in a 20,000 cfm venturi, combined with the storage building ventilation stream and sent to a spray tower. The storage building ventilation air is sent directly to the spray tower. Total fluoride emissions are 127 pounds per hour with existing controls.

The retrofit project involves the removal of the existing scrubbers and the installation of a new control system consisting of preliminary cyclonic spray towers on the ventilation streams from the production and storage areas followed by a secondary cyclonic spray tower treating the combined effluent streams. This system will reduce fluoride emissions to 4.6 pounds per hour which is equivalent to the emission guideline.

Retrofit controls will be located as shown in Figure 6-15. Moderate rearrangement of the ductwork is necessary to install the cyclonic spray towers. Two new fans will be required because of the higher pressure drop associated with the retrofit system. Existing water lines and pumps will be used to supply the preliminary scrubbers. A 14-inch line will be installed to provide 1725 gpm of pond water for the secondary scrubber. Spent scrubbing water will be recycled to the gypsum pond in the existing drainage system. Treated gases will be emitted from a newly installed 75 foot stack.


GYPSUM POND
1300'
MIXER CONE AND DEN VENTILATION
STORAGE BUILDING VENTILATION
STACK
ROP-TSP PRODUCTION
ROP-TSP STORAGE
100'
375'
100'

○ — CYCLONIC SPRAY TOWER SCRUBBER

Figure 6-15. RETROFIT CONTROL EQUIPMENT LAYOUT FOR MODEL ROP-TSP PLANT.

Table 6-41 lists the major cost items involved in this retrofit project. Operating conditions for the three cyclonic spray towers are provided in Table 6-42. Retrofit costs are estimated in Table 6-43.

Table 6-41. MAJOR RETROFIT ITEMS FOR MODEL ROP-TSP PLANT

1. Rearrangement of ductwork - removal of venturi and spray tower from service and connection of three cyclonic spray towers and stack. Requirements are 50 feet of 42-inch duct and 125 feet of 96-inch duct.

2. Water line connecting gypsum pond with cyclonic spray tower treating the combined effluent streams from the production and the storage area - 1600 feet of 14-inch pipe.

3. Centrifugal pump - 1725 gpm, 167 feet total dynamic head (TDH), 125-horsepower motor.

4. Removal of venturi and spray tower.

5. Centrifugal fan for the storage building ventilation system - 125,000 SCFM, 514 feet TDH, 250 horsepower motor. Centrifugal fan for the combined effluent streams - 150,000 SCFM, 461 feet TDH, 175 horsepower motor.

6. Three cyclonic spray tower scrubbers. When using pond water specified in Table 6-7 and treating the effluent streams describ in Table 6-23, scrubbers are required to obtain the performance indicated in Table 6-42.

7. Stack - 75 feet tall, 9 feet diameter.

8. Supports and foundations.

Table 6-42. OPERATING CONDITIONS FOR CYCLONIC SPRAY TOWER SCRUBBERS FOR MODEL ROP-TSP PLANT (550 Tons/Day P_2O_5)

	Mixing cone and den ventilation stream	Storage building ventilation stream	Combined streams
Gas to scrubber			
Flow, SCFM	25,000	125,000	150,000
Flow, DSCFM	24,500	122,500	145,500
Flow, ACFM	28,400	128,200	154,000
Temp., °F	140	85	85
Moisture, Vol. %	2	2	3
Fluoride (as F), lb/hr	307	396	50.5
Fluoride (as F), ppm	4,000	1,000	107
Gas from scrubber			
Flow, SCFM	25,300	126,000	150,000
Flow, DSCFM	24,500	122,500	145,500
Flow, ACFM	27,500	128,500	153,000
Temp., °F	115	80	80
Moisture, vol. %	3	3	3
Fluoride (as F), lb/hr	20.5	30	4.6
Fluoride (as F), ppm	260	76	9.7
Fluoride removal, wt %	93	92.5	91
Estimated y', ppm	0.8	0.8	0.8
Estimated NTU required	2.7	2.6	2.5

Table 6-43. RETROFIT COSTS FOR MODEL ROP-TSP PLANT
(550 Tons/Day P_2O_5) November 1974

		Cost ($)
A.	Direct Items (installed)	
	1. Centrifugal spray tower scrubbers (3)	300,000
	2. Ductwork	25,000
	3. Piping	29,100
	4. Pump and motor	22,200
	5. Centrifugal fans and motors	54,400
	6. Removal of old equipment	12,500
	7. Stack	44,000
	8. Performance test	4,000
	Total Direct Items	491,200
B.	Indirect Items Engineering construction expense, fee, interest on loans during construction, sales tax, freight insurance (50% of A.)	245,600
C.	Contingency (25% of A.)	122,800
D.	Total Capital Investment	859,600
E.	Annualized Costs	
	1. Capital charges	140,100
	2. Maintenance	23,400
	3. Operating labor	6,000
	4. Utilities	48,600
	5. Taxes, insurance, administrative	34,500
	Total Annualized Costs	252,600

6.4 IMPINGEMENT SCRUBBER

Impingement scrubbers are primarily particulate collection devices but they also possess some absorption capability and have been used with limited success to treat effluent streams from wet-process acid and diammonium phosphate plants. The Doyle scrubber pictured in Figure 6-16 is the type most commonly used by the fertilizer industry.

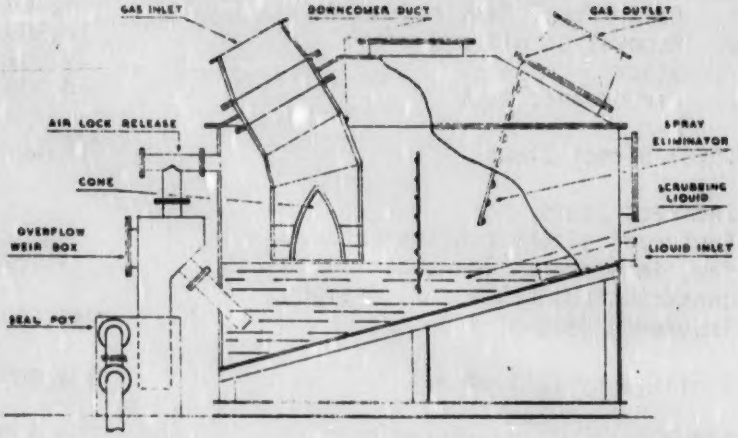

GAS INLET
DOWNCOMER DUCT
GAS OUTLET
AIR LOCK RELEASE
SPRAY ELIMINATOR
CONE
SCRUBBING LIQUID
OVERFLOW WEIR BOX
LIQUID INLET
SEAL POT

FIGURE 6-16. DOYLE SCRUBBER.

Effluent gases are introduced into the scrubber as shown in Figure 6-16. The lower section of the inlet duct is equipped with a axially located cone that causes an increase in gas stream velocity prior to its impingement on the surface of the pond. The effluent gases contact the pool of scrubbing liquid at a high velocity and undergo a reversal in direction. Solids impinge on the liquid surface and are retained while absorption of gaseous fluorides is promoted by the interphase mixing generated by impact. Solids handling capacity is high, however, absorption capability is very limited.[33]

6.5 SUMMARY OF CONTROL OPTIONS

Sections 6.1 through 6.4 have examined the operational characteristics of several scrubber designs commonly used in the phosphate fertilizer industry. Only the spray-crossflow packed bed scrubber is capable of providing the degree of fluoride control required to meet SPNSS emission levels in all cases. In certain cases, cyclonic spray tower scrubbers will meet the standards, but only at a higher cost as the ROP-TSP retrofit example illustrates (Table 6-44). Although retrofit costs for installing venturi scrubbers in a DAP plant were lower than those for spray-crossflow packed bed scrubbers, there is no data available which substantiates that a venturi scrubber alone can achieve SPNSS emission levels. The primary value of venturi scrubbers in fluoride control is their higher solids handling capacity. This feature is exploited in several spray-crossflow packed bed scrubber designs which incorporate a preliminary venturi scrubber.

Table 6-44. ESTIMATED TOTAL CAPITAL INVESTMENT AND ANNUALIZED COST FOR DAP AND ROP-TSP RETROFIT MODELS USING SPRAY-CROSSFLOW PACKED BED AND ALTERNATIVE SCRUBBERS. November 1974.

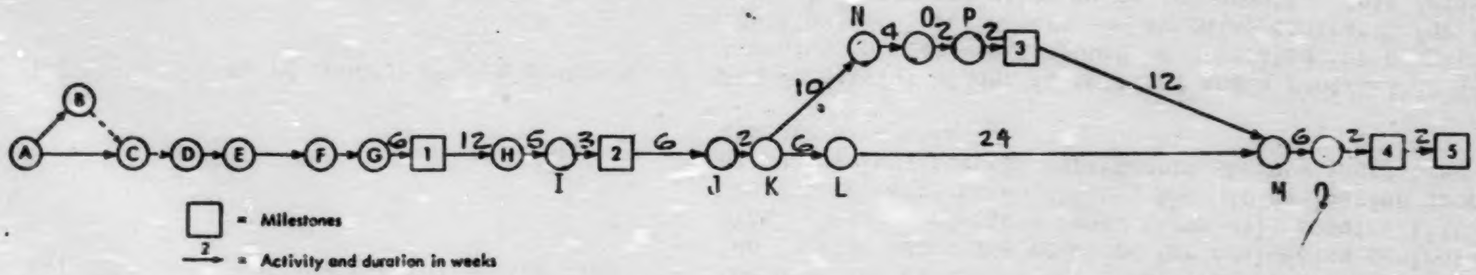
Facility	Type of Scrubber	Capacity (tons/day P_2O_5)	Total Capital Investment	Annualized Cost
DAP	Spray-crossflow packed bed	500	$733,100	$194,100
DAP	Venturi	500	558,800	163,500
ROP-TSP	Spray-crossflow packed bed	550	802,100	214,900
ROP-TSP	Cyclonic spray tower	550	859,600	252,600

6.6 DESIGN, INSTALLATION, AND STARTUP TIMES

This section discusses the time required to procure and install a wet scrubber on a phosphate fertilizer operation. Actual time requirements can vary tremendously depending upon such factors as space limitations, weather conditions, lack of available utilities, delays in equipment delivery, and lack of engineering data. The information presented in this section, has to a limited extent, attempted to take such factors into consideration. Since these estimates are general, however, they should be used primarily as a guideline and may be modified as dictated by specific circumstances.

Figure 6-17 identifies the various steps involved in the procurement and installation of a wet scrubber on a wet-process phosphoric acid plant. It also provides an estimate of the total time requirement of the project. In estimating this time requirement, it was assumed that those activities leading up to the finalization of control equipment plans and specifications had been completed prior to the initiation of the retrofit project. The individual steps shown in Figure 6-17 are explained in more detail in Table 6-45.

FIGURE 6-17. TIME SCHEDULE FOR THE INSTALLATION OF A WET SCRUBBER ON A WET-PROCESS PHOSPHORIC ACID PLANT[34]



MILESTONES

		ELAPSED TIME (WEEKS)
1	Date of submittal of final control plan to appropriate agency.	6
2	Date of award of control device contract.	26
3	Date of initiation of on-site construction or installation of emission control equipment.	52
4	Date by which on-site construction or installation of emission control equipment is completed.	72
5	Date by which final compliance is achieved.	74

ACTIVITIES

Designation		Designation	
A-C	Preliminary investigation	J-K	Review and approval of assembly drawings
A-B	Source tests	K-L	Vendor prepares fabrication drawings
C-D	Evaluate control alternatives	L-M	Fabricate control device
D-E	Commit funds for total program	K-N	Prepare engineering drawings
E-F	Prepare preliminary control plan and compliance schedule for agency	N-O	Procure construction bids
F-G	Agency review and approval	O-P	Evaluate construction bids
G-1	Finalize plans and specifications	P-3	Award construction contract
1-H	Procure control device bids	3-M	On-site construction
H-I	Evaluate control device bids	M-Q	Install control device
I-2	Award control device contract	Q-4	Complete construction (system tie-in)
2-J	Vendor prepares assembly drawings	4-5	Startup, shakedown, preliminary source test

Table 6-45. DESCRIPTION OF INDIVIDUAL ACTIVITIES INVOLVED IN THE PROCUREMENT, INSTALLATION, AND STARTUP OF CONTROL EQUIPMENT.[35]

ACTIVITY CODE	ACTIVITY DESCRIPTION	DETAILS OF ACTIVITY AND ESTIMATED TIME REQUIREMENT
G-1	Finalize plans and specification	The control system is specified in suffient detail for control equipment suppliers and contractors to prepare bids. A final control plan summarizing this information is also prepared for submittal to the appropriate agency. Two to six weeks are allocated for this activity. The variation is dependent on the magnitude and complexity of the project.
1-H	Procure control device bids	Transmittal of specifications for the control device and request for bids from suppliers. A minimum time of four weeks is required to procure bids on small jobs. A maximum of twelve weeks should be allowed for large non-standard units. Initial vendor quotations frequently do not match bid specifications, thereby requiring further contacts with each bidder.
H-I	Evaluate control device bids	The bids are evaluated and suppliers are selected. Two to five weeks are required for evaluating control device bids. Small, privately owned firms will require little time. whereas in large corporations, the bid evaluation procedure often involves several departments thereby increasing the time requirements.
I-2	Award control device contract	The successful bidder is notified and a contract is signed. A minimum of two weeks should be allocated for preparing the final contract papers and awarding contracts for the control device and other major components. This activity will take longer in large corporations where examination and approval of the contract by several departments is required.

Table 6-45 (continued). DESCRIPTION OF INDIVIDUAL ACTIVITIES INVOLVED IN THE PROCUREMENT, INSTALLATION, AND STARTUP OF CONTROL EQUIPMENT.[35]

ACTIVITY CODE	ACTIVITY DESCRIPTION	DETAILS OF ACTIVITY AND ESTIMATED TIME REQUIREMENT
2-J	Vendor prepares shop drawings	The vendor prepares the assembly drawings for the control device. For the smaller and more common types of control equipment, standard shop drawings which apply to several control equipment size ranges may be used with the appropriate dimensions underlined or otherwise indicated. For larger devices, it may be necessary to prepare drawings specifically for the project at hand. The drawings are mailed to the client for his approval prior to initiating fabrication drawings. Depending on the complexity and originality of the design, the time required by the vendor to submit assembly drawings could vary from few weeks to few months. Two to six weeks are estimated for this activity.
J-K	Review and approval of assembly drawings	The client reviews the assembly drawings and gives approval to begin fabrication drawings. The client also uses the assembly drawings to prepare the necessary engineering drawings One to two weeks are sufficient for review and approval of assembly drawings. The longer time is required for any delay in approval as a result of revisions and modifications.
K-L	Vendor prepares fabrication drawings	Upon receipt of approval from client to proceed with construction of the control device, the vendor prepares fabrication or shop drawings which will be used in the manufacturing and assembling of the control equipment. Three to eight weeks are normally required for this task.

Table 6-45 (continued). DESCRIPTION OF INDIVIDUAL ACTIVITIES INVOLVED IN THE PROCUREMENT, INSTALLATION, AND STARTUP OF CONTROL EQUIPMENT.[35]

ACTIVITY CODE	ACTIVITY DESCRIPTION	DETAILS OF ACTIVITY AND ESTIMATED TIME REQUIREMENT
K-N	Prepare engineering drawings	This is the time which is required by the client (or his consultant) to prepare an engineering drawings package for use by the construction company for installing foundations, structures, ductwork, electrical outlets and any other items not supplied with the control device. The drawings will also show the location and tie-in of the control device. Estimated engineering time for the project in question is 10 weeks.
L-M	Fabrication of control device	On small size control devices which can be shop assembled, this activity represents the fabrication, assembly, and delivery of the control unit to the site. On large field erected control devices, the time shown for this activity indicates the fabrication and delivery of the first component to the site. Delivery of the remaining components continues throughout the construction phase. The duration of this activity should be estimated after consultation with manufacturers of the appropriate air pollution control device. Estimate time requirement for this project is 24 weeks.
N-O	Procure construction bids	The bid package specifying the scope of work and specificatio of materials and including the drawings are mailed to selecte contractors. During this period, the contractors prepare the bids for needed material and labor to install all ductwork, piping, utilities, and control equipment. A minimum of four weeks should be allocated for obtaining bids from the contractors.

Table 6-45 (continued). DESCRIPTION OF INDIVIDUAL ACTIVITIES INVOLVED IN THE PROCUREMENT, INSTALLATION, AND STARTUP OF CONTROL EQUIPMENT.[35]

ACTIVITY CODE	ACTIVITY DESCRIPTION	DETAILS OF ACTIVITY AND ESTIMATED TIME REQUIREMENT
O-P	Evaluate construction bids	Construction bids are evaluated and the successful bidder selected. Two weeks are estimated for this activity.
P-3	Award construction contract	Construction contract is prepared. In large corporations, it is reviewed and approved by several departments prior to its submission to the successful contractor. Two weeks are allowed for this activity.
3-M	On-site construction	This consists of site clearance, pouring of the foundation, erecting structural members, ductwork, and installation of auxiliary equipment. Twelve weeks were estimated for this activity.
M-Q	Install control device	This activity is essentially an extension of the preceding construction work. The time is primarily allocated for installation of a shop assembled (or modular) control device. In case of field erected unit, it represents the time which i required to complete the installation of the remaining components as they arrive on site. The installation time for this case is estimated to be six weeks.

Table 6-45 (continued). DESCRIPTION OF INDIVIDUAL ACTIVITIES INVOLVED IN THE PROCUREMENT, INSTALLATION, AND STARTUP OF CONTROL EQUIPMENT.[35]

ACTIVITY CODE	ACTIVITY DESCRIPTION	DETAILS OF ACTIVITY AND ESTIMATED TIME REQUIREMENT
0-4	Complete construction (system tie-in)	Tying the control device into the process requires that the process be shut down. This shut down is usually scheduled so that it will have the least impact on the operation. The contractors responsibility usually ends at this point when the client and the vendors representativ accept the construction as being complete. Two to six week are allocated for tie-in. In large installations where the process cannot be conveniently shut down at the end of construction phase, longer times may be required.
4-5	Start up, shakedown, source test	The process is brought back on-line and any unforeseen problems with the control system are resolved during this time. Source testing may be performed to determine if performance of the system is acceptable. Depending on the type of control device installed, start up, shake down, and preliminary source testing would require from two weeks for small and simple installation to about eight weeks for a la and complicated system.

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7. ECONOMIC IMPACT

7.1 INTRODUCTION

This section describes the economic impact of adopting regulations that require control of fluoride emissions from existing wet-process phosphoric acid, superphosphoric acid, diammonium phosphate, run-of-pile triple superphosphate, and granular triple superphosphate facilities. The costs shown in Table 7-1 are based upon the installation and operation of control equipment described in chapter 6.1.3. Installation of other, less efficient control equipment is not expected to result in any significant reduction in the economic impact incurred. The capital costs and annualized costs of installing control equipment represent expenditures needed to achieve the emission guidelines shown in Table 1-2, but would also apply to the adoption of less stringent fluoride emission regulations.

The economic impacts have been developed on a process-by-process basis since the national or industry-wide impact will be dependent upon the collective actions of the states. To provide a perspective on the significance of the costs incurred by adopting fluoride emission regulations, they are related to unit production and product sales price (Table 7-1). Additional insight on potential impacts related to costs are given by a discussion on potential plant closures. Criteria are presented that describe circumstances that could result in plant closures, and the number of closures within the industry that would result if all states adopted fluoride emission regulations is estimated.

The information presented in this chapter is intended to assist states in deciding on the advisability of adopting fluoride regulations.

It is not expected that these emission guidelines would be appropriate for all existing facilities.

7.2 IMPACT ON MODEL PLANTS

The total capital investment and annualized control cost obtained from section 6.1.3.1 for each of the model facilities is presented in Table 7-1 on a plant basis, on a unit product basis, and as a percentage of the product sales price. For purposes of this analysis, it is assumed that the wet-process acid plant sells all acid production at prevailing merchant acid prices. The estimated control costs for superphosphoric acid, diammonium phosphate, and triple superphosphate plants reflect the retrofit requirements of both the individual production facility and an associated wet-process acid plant which produces the required intermediate phosphoric acid. The captive acid plants are assumed to be sufficiently sized to supply the needs of the various production units. For example, the SPA plant is associated with a 300 ton P_2O_5/day acid plant while the DAP plant requires a 500 ton/day unit. Control costs for the captive units were obtained by prorating the costs developed for the model acid plants.

A more detailed analysis of the potential financial effects of control costs upon the phosphate industry could be obtained by calculating the changes in profits and cash incomes for all plants or firms in the industry if the necessary information were available. Diammonium phosphate and granular triple superphosphate are the more popular products sold and their processing will incur the higher control costs on a unit basis. Industry statistics, representative of 1973 performance, indicate that after-tax profit margins ranged

TABLE 7-1

SUMMARY OF RETROFIT CONTROL COST REQUIREMENTS FOR VARIOUS PHOSPHATE FERTILIZER MANUFACTURING PROCESSES

End Product	Phosphoric Acid	Super-Phosphoric Acid	DAP	ROP-TSP (Case A)	ROP-TSP (Case B)	GTSP
Design Rate, TPD (P_2O_5 Basis)	500	300	500	550	550	400
Control Capital, $	229,000 272,000	264,000	984,000	968,000	1,542,000	1,386,000
Sales Price ($ per ton product)	105	152	145	126	126	130
Annualized Costs						
a. Total, $	62,000 74,000	69,000	262,000	260,000	414,000	370,000
b. Unit Basis ($ per ton product)	.20 - .24	.52	.73	.66	1.05	1.29
c. As a % of Sales Price	0.2	0.3	0.5	0.5	.8	1.0

Source of Price Quotations - Chemical Marketing Reporter, November 4, 1974.

from 5 to 6 percent of sales and approximately doubled these percentages in 1974. Against this level of profitability, control costs as shown in Table 7-1 appear to have minimal impact on a plant typical of this profit performance. As long as product prices are unrestricted (the Cost of Living Council removed price ceilings on domestic fertilizers on October 25, 1973) and plant utilization remains at the current level of approximately 90 percent, control costs could be absorbed by the industry without any price increases. On the other hand, price increases to pay for the costs would be minimal.

An objective of this analysis is to highlight where the implementation of the emission guidelines might impose an economic burden upon plants. A scenario for possible plant closures could be presented in this fashion: overcapacity in spite of growing demand develops in a particular segment of the industry resulting in underutilization at rates near 75 and 80 percent of capacity. Prices and profits subsequently decline. In such a situation, plants would probably close; however, the question is to what extent would the impact of retrofit controls be responsible for plant closures. In section 7.3, criteria are presented which can be used to pinpoint the extent of plant closures.

7.3 CRITERIA FOR PLANT CLOSURES

Reasons for closing a facility are usually traced to the absence of profitability for a specific site or facility. Managers of existing plants faced with increased capital requirements for continuity of operations will have to decide whether the incremental investment will "save" future cash income that otherwise would be lost by ceasing operations. Plant managers will have the following options in such a situation:

1. Undergo increased capital expenditures on the existing plant.
2. Shut down the plant and discontinue business.
3. Shut down the plant and replace it with a new plant.

The selection of an option is based on an interest or opportunity cost for employing the required capital. There is usually a minimum return that a plant manager will accept for employing funds--interest cost for borrowing money or the interest cost of investing in short term obligations. Since there is a risk with employment of capital, businesses will require a higher rate of return for investing of funds. A familiar tool for analyzing investments involves the determination of the sum of all future cash flow (income) streams over a projected time span discounted (with the appropriate interest rate) to the present. If the sum of these discounted residuals exceeds intended cash outlay for investment, resulting in a positive term for net present value, than the investment will be a good choice. Conversely, if the discounted present value of projected cash flow streams results in a negative value, then the proposed investment will be rejected.

The managerial tool of discounted cash flow analysis can be applied to the retrofitting of control equipment to existing plants in this manner. If the existing operations can only be continued in the future by meeting a standard, then the investing of the control capital has to be evaluated on the basis of the value of the future income derived from continuing the operation of the present plant. The merit of continuing operations after retrofitting a plant must be evaluated in retrospect with the alternatives of discontinuing operations and building a new plant.

Guidelines for pinpointing plants as candidates for closure are presented as follows. First, new plants to replace existing plants of the comparable model size described in Table 7-1 would require some \$10 to \$20 million. In no instance could the construction of a new plant be a better alternative than retrofitting controls requiring the magnitude of capital, or even twice the values, shown in Table 7-1. On the other hand, plants that have small or negative cash incomes prior to retrofitting would certainly close. Plants that have small or negative profits (after deducting depreciation charges) would eventually become candidates for closure upon termination of their depreciation schedules and subsequent increased tax liability.

The type of plants that would most likely face these circumstances are the following:

1. Small plants which generally suffer from the usual economies of scale of production--less than 170,000 tons-per-year capacity.[1]
2. Old plants which generally have outlived their useful or economic lives--twenty years or more.
3. Plants isolated from raw materials--particularly diammonium phosphate plants that purchase merchant phosphoric acid and ammonia.
4. Plants likely to suffer from a shift in the overall market structure as a result of external forces.

Financial data on an individual plant basis necessary to evaluate the impact of retrofit controls are unfortunately unavailable. Hence, plant closures can be estimated only from a categorical approach, which classifies plants that possess characteristics of the nature of those discussed above. Any estimate of plant closures has to be presented with the usual qualifications.

7.4 IMPACT ON THE INDUSTRY

At the present time, the condition of the fertilizer industry is healthy. Prices and profits in 1974 were the highest they have been in years. The U.S. industry has become a leader in phosphate processing technology and benefits from world trade in both rock and concentrated phosphates. This position became more pronounced recently, in spite of the fracture in the international monetary structure and concurrent high inflation. When the Cost of Living Council lifted price ceilings on October 25, 1973, domestic prices heretofore constrained by CLC immediately arose 60 percent on the average reflecting the foreign demand for domestic phosphate products. Demand for fertilizers to increase agricultural production and yields has been strong and will continue to be so, in spite of fluctuating international currency values. Projected long-term demand for phosphate nutrients is expected to grow at an annual rate of 5-6 percent.[2]

Historically, the fertilizer industry has experienced cyclic patterns of overexpansion followed by plant shutdowns and product price cutting. New phosphoric acid plant expansion scheduled to come on stream in 1975-1976 may result in short term price declines until increases in consumer demand restores equilibrium with capacity. In anticipation of overexpansion, producers will probably curtail construction activity in the period beginning in 1976-1977. However, during this slack period, retrofitting of existing plants for controls will be required in accordance with implementation plans. Therefore, these retrofit projects should not hinder new construction. Rather than resulting in plant closures, requirements for retrofitting fluoride emission control systems will probably encourage some improvements of marginal plants.

The nature of the impact of the 111(d) regulations for the fertilizer industry will be geographical in scope. The state of Florida, where most of the industry is located, has adopted regulations for the existing industry that are equivalent in most instances to the emission guidelines. Most of the remaining states with phosphate process facilities have no emission standards.

The greatest control cost - on a unit basis - for any process subject to standards is for the combination of processing and storage of granular triple superphosphate. However, 75 percent of the industry capability in GTSP production will be required to meet the emission guideline by July 1975 regardless of Federal action. Since a large portion of the production facilities will not require additional retrofit controls, the impact upon the industry doesn't appear severe. For run-of-pile triple superphosphate, the conclusion would be similar to the GTSP as some 60 percent of the industry will be adequately controlled because of state standards.

The one segment of the industry where a wide-scale effort in retrofitting would be required is for diammonium phosphate plants. Some 60 percent of industry capacity would be expected to retrofit as a result of Federal regulations. Control costs for this process, however, would amount to only 0.5 percent of sales. These costs alone are not sufficient to close any plants.

Diammonium phosphate plants which incur water abatement costs as great or greater than fluoride emission control costs would be likely candidates for plant closures.[3] There is no specific information concerning plants which may fall into this category. The only definitive statement that can be made is that those affected will be outside the state of Florida and may amount to 3 to 5 plants, or approximately 10 percent of the total DAP manufacturing capacity.

With regard to triple superphosphate plants, 1 to 3 plants (outside Florida) may close as a result of implementing the recommended emission guidelines for control of gaseous fluoride. This is likely to occur in a geographical region where there is an oversupply of phosphate processing capacity. An abundant supply of low-cost sulfuric acid derived from non-ferrous smelters in the Rocky Mountains area could be an incentive for construction of new phosphate facilities, ultimately resulting in oversupply and price-cutting. Triple superphosphate capacity does appear to be expanding rapidly in this area with a new 340,000 ton-per-year plant coming on-stream in 1975-1976.

Most of the control costs associated with a TSP complex are for the solids manufacture and storage. Therefore, the closure of a TSP facility as implied above does not mean that the entire complex will be shut down. The plant manager has several options--(1) sell merchant acid, (2) convert to mixed fertilizers, or (3) produce diammonium phosphate. However, if the same plant manager is faced with installing water abatement facilities, the overall abatement costs will affect the entire facility.

7.5 IMPACT ON EMPLOYMENT AND COMMUNITIES

The fertilizer industry is generally recognized as a capital intensive industry; in other words, labor requirements for production work and plant supervision are small, relative to plant sales. Usually, those plants that may be affected by implementation of the emission guidelines are widely dispersed throughout the United States. Only in central Florida does the fertilizer industry represent a substantial portion of overall community economic activity and employment.

For purposes of illustrating the effects of plant closures on employment, the shutdown of 1 to 3 triple superphosphate plants cited in Section 7.4 might result in the loss of 10 to 50 jobs.[4] Only those jobs directly associated with the triple superphosphate plants would be affected. Employment in supporting activities such as rock mining, phosphoric acid production, and transportation services would remain unaffected.

7.6 SUMMARY

An optimistic outlook for the phosphate fertilizer industry in the next few years has been presented, but such an appraisal must be cautionary after reviewing the historical chronic cyclic patterns of product shortages and oversupply. Assuming that oversupply conditions may occur in the next few years, some estimates of plant closures have been made. In the triple superphosphate sector of the industry, as many as three plants could close as a direct result of the states adopting the emission guidelines. In the diammonium phosphate a combination of expenditures for retrofitting both fluoride emission controls and water effluent controls may result in as many as five plant closures, or 10 percent of industry capacity.

However, fluoride emission controls alone would not cause these closures. Associated costs for fluoride emission controls for wet-process phosphoric acid plants that do not have attendant DAP or TSP processes will not warrant plant closures. Similarly, costs for superphosphoric acid plants do not present any apparent problems.

The number of predicted closures reflects the adoption of the emission guidelines by all states; therefore, it reflects the maximum number of closures that may occur.

7.7 REFERENCES

1. David, Milton L., J.M. Malk, and C.C. Jones. Economic Analysis of Proposed Effluent Guidelines for the Fertilizer Industry. Development Planning and Research Associates, Inc. Washington, D.C. Publication Number EPA 230-1-73-010. November 1973. p. VI-12 to VI-15.

2. U.S. Industrial Outlook 1972 - With Projections to 1980. U.S. Department of Commerce. Washington, D.C. Publication Number BOC-704-08-72-005. p. 174-175.

3. Reference 4, p. V-13 to V-18.

4. Reference 4, p. VI-26.

8. EMISSION GUIDELINES FOR EXISTING PHOSPHATE FERTILIZER PLANTS

8.1 GENERAL RATIONALE

These emission guidelines represent the same degree of control as is required by the standards of performance promulgated for new plants [wet-process phosphoric acid, superphosphoric acid, diammonium phosphate, run-of-pile triple superphosphate (production and storage), and granular triple superphosphate (production and storage)]. The emission guidelines were developed after consideration of the following factors:

1. The degree of emission reduction achievable through the application of the best adequately demonstrated system of emission reduction (considering cost).
2. The technical and economic feasibility of applying the best demonstrated technology to existing sources.
3. The impact of adopting the emission guidelines on annual U. S. fluoride emissions.
4. The environmental, energy and economic costs of the emission guidelines.

Identification of the best demonstrated control technology was accomplished first. During the development of standards of performance for new facilities in the phosphate fertilizer industry, the spray-crossflow packed bed scrubber was found to represent the best demonstrated control for total fluoride emissions. Historically, the spray-crossflow packed bed scrubber was developed to control fluoride emissions from the phosphate fertilizer industry. From this viewpoint, it is not unusual that this scrubber design is the best demonstrated control technology. Many of the spray-crossflow packed bed scrubbers tested by EPA were retrofitted. For this reason, spray-crossflow packed bed scrubbers are recognized as the best demonstrated control technology for both new and existing plants.

Alternative fluoride control technologies, such as the venturi and cyclonic spray tower scrubbers, can only provide approximately two transfer units for fluoride absorption unless two or more are used in series, at multiplied costs. Spray-crossflow packed bed scrubbers are not limited by the number of transfer units which they can provide; in practice, five to nine transfer units per scrubber are provided. Control of gas streams with high particulate loadings has caused a plugging problem for spray-crossflow packed bed scrubbers in the past. However, use of a built-in venturi scrubber and other improvements in spray-crossflow packed bed scrubber design have eliminated this problem. In addition, all current fluoride control technologies involve some type of scrubbing system, and consequently, they share any plugging tendencies, as well as similar costs and energy requirements. With these considerations in mind, it is not unreasonable to base fluoride emission guidelines on the one clearly superior scrubbing technology.

Evaluation of the problems and costs associated with a retrofit project is complicated by the lack of actual data. Some of the facilities equipped with spray-crossflow packed bed scrubbers installed the units as part of the original plant design. Retrofit information that is available is usually incomplete because of changes in plant management and lack of cost breakdowns. Retrofit models were therefore developed to evaluate the technical and economic feasibility of installing spray-crossflow packed bed scrubbers on existing WPPA, SPA, DAP, ROP-TSP, GTSP processing, and GTSP storage facilities. The retrofit model approach was meant to estimate costs for an average plant and to clarify the technical problems involved in a typical retrofit project. No technical problems, other than space limitations, were foreseen for the average plant. In all cases, the magnitude of the estimated retrofit costs is minimal as is discussed in Section 7.

Table 9-1 indicates the impact of the emission guidelines on annual U.S. fluoride emissions. Adoption of the emission guidelines would result in emission reductions ranging from 50 percent for GTSP storage facilities to 90 percent for ROP-TSP plants. Overall emissions from the affected facilities would be reduced by 75 percent.

Environmental and energy costs associated with the emission guidelines are minimal. With current spray-crossflow packed bed scrubber designs, gypsum pond water can be used as the scrubbing medium to meet the emission guidelines in practically all cases. In the rare case where the partial pressure of fluoride out of pond water is high, the emission guidelines can still be met. The aliquot of water sent to the final section of scrubber packing may be fresh or limed water. This aliquot will only be a small fraction of the total water to the scrubber and will contain only a small fraction of the total fluoride absorbed in the scrubber. This implies that no additional effluent need be created. Any solids generated by fluoride scrubbing (e.g., in the WPPA process) would go to the gypsum pond and cause no more than a 0.06 percent increase in the amount of solids normally produced.

The estimated total annual incremental electrical energy demand which would be created by fluoride control to meet the emission guidelines is only 38.7 X 10^6 KWH/yr. This is equivalent to the amount of energy required to operate only one 300 tons/day P_2O_5 SPA plant by the submerged combustion process 115 days/yr.

8.2 EVALUATION OF INDIVIDUAL EMISSION GUIDELINES

8.2.1 Wet-Process Phosphoric Acid Plants

Fluoride Emission Guideline

0.01 grams of fluoride (as F^-) per kilogram of P_2O_5 input to the process.

Discussion

The emission guideline is equal to the standard of performance for new plants. Control to the level of the guideline would require removal of 99 percent of the fluorides evolved from the wet-acid process. A spray-crossflow packed bed scrubber is capable of providing this collection efficiency.

Rationale

The economic impact of the emission guideline on the industry is negligible. Approximately 53 percent of the existing wet process acid plants, accounting for 74 percent of the production capacity, are either sufficiently controlled at present to meet an emission level of 0.01 grams F/kilogram P_2O_5 or will be required to attain that level of control regardless of the proposed emission guideline. This estimate is based on the assumption that all wet-process acid plants built since 1967 have installed controls capable of meeting an emission level of 0.01 grams of fluoride per kilogram P_2O_5 input as part of the original plant design.

The retrofit costs for those plants that are affected, approximately $230,000 for a 500 ton P_2O_5/day facility, can be successfully absorbed within the existing cost structure. Annualized control costs for an average sized plant, including capital charges, amount to approximately 0.2 percent of sales.

Relaxation of the guideline to allow emission increases of 50 to 100 percent would not allow additional control options or appreciably reduce retrofit costs for the following reasons:

a. Only a packed bed scrubber is capable of providing the required fluoride removal efficiency ≈ 99 percent. A tenfold increase in the emission guideline would be required to allow the use of other commonly used scrubber designs - venturis, cyclonic spray towers, etc. with 85-90 percent collection efficiency.

b. Packed bed scrubber cost will not vary significantly with moderate changes in packing depth. The cost of additional packing to increase scrubber efficiency is minor compared to overall control costs.

Estimated impact of the emission guideline on annual fluoride emissions is significant - 73 percent reduction.

8.2.2 Superphosphoric Acid Plants

Fluoride Emission Guideline

0.005 grams of fluoride (as F^-) per kilogram of P_2O_5 input to the process.

Discussion

The emission guideline for existing SPA plants is equal to the standard of performance for new facilities. Control to the level of the guideline would require removal of approximately 90 percent of the fluorides now being emitted from SPA plants using the submerged combustion process. A spray-crossflow packed bed scrubber is capable of providing this performance. Three designers of control equipment have submitted proposals to one operator for control to the level of the emission guideline; venturi and other designs were quoted, including the spray-crossflow packed bed scrubber (1). Plants using the vacuum evaporation process (79 percent of the SPA industry) will require no additional control.

Rationale

Impact on the industry is negligible. The two existing plants using the submerged combustion process could be required to add retrofit controls.

Existing submerged combustion plants are capable of meeting the emission guideline by treating the exhaust stream from controls with a spray-crossflow packed bed scrubber. This scrubber can be added to any existing mist separators, baffles, and spray chambers, as was assumed in the SPA retrofit model, Figure 6-5.

Retrofit costs are expected to be acceptable ($114,000 for a 300 ton per day plant). Annualized control costs, including capital charges, amount to only 0.3 percent of sales.

Relaxing the emission guideline to allow a three-fold increase in emissions (0.015 grams F/kilogram P_2O_5) would be required to accommodate the use of venturis and cyclonic spray towers, if the retrofit costs are to remain about the same.

8.2.3 Diammonium Phosphate Plants

Fluoride Emission Guideline

0.03 grams of fluoride (as F^-) per kilogram of P_2O_5 input to the process.

Discussion

The emission guideline for existing DAP plants is equal to the standard of performance for new facilities. Control to the level of the guideline would require removal of approximately 85 percent of the fluorides evolved from the DAP process. Spray-crossflow packed bed scrubbers, added to any existing venturis, are capable of providing the required collection efficiency. As pointed out in section 8.1, new designs for these scrubbers are available and are expected to overcome problems formerly associated with plugging by excessive particulates (2).

Rationale

Relaxing the emission guideline to allow the use of alternative scrubber technologies would increase fluoride emissions to the atmosphere by 49 tons per year, a 50 percent increase.

Retrofit costs (733,000 for a 500 ton P_2O_5/day plant) are not considered excessive. Annualized cost, including capital charges, would amount to 0.5 percent of sales.

Impact of applying the emission guideline on fluoride emissions from U. S. DAP plants is significant - a 65 percent reduction (160 tons/year.

8.2.4 Run-of-Pile Triple Superphosphate Production and Storage Facilities

Fluoride Emission Guideline

0.1 gram of fluoride (as F^-) per kilogram of P_2O_5 input to the process.

Discussion

The emission guideline is equal to the standard of performance for new facilities. Only 40 percent of the industry is directly affected by the emission guideline.

Compliance with a 0.1 gram F per kilogram P_2O_5 emission level would require collection of about 99.2 percent of the fluorides evolved from the process. This efficiency can be obtained by a two stage system using venturis and a spray-crossflow packed bed scrubber.

Rationale

Economic impact on the industry is moderate. Only 40 percent of the industry is directly affected by the emission guideline. The remaining 60 percent will be required to meet more stringent State regulations.

No additional control options would be made available by relaxing the emission guideline by 50 to 100 percent. It would be necessary to triple the emission guideline to allow the use of a venturi or cyclonic spray tower as the secondary scrubber.

Retrofit costs ($800,000 for a typical 550 ton P_2O_5/day plant to $1,371,000 for the extreme case) are not considered excessive. Annualized control costs, including capital charges, amount to 0.50 to 0.80 percent of sales. Although these costs are more severe than retrofit costs for most other sources, they are expected to be manageable.

The emission guideline would reduce annual fluoride emissions from existing ROP-TSP plants by 88 percent.

8.2.5 Granular Triple Superphosphate Production Facilities

Fluoride Emission Guideline

0.1 gram fluoride (as F^-) per kilogram of P_2O_5 input to the process.

Discussion

The fluoride emission guideline is equal to the standard of performance for new facilities. Compliance with the emission guideline would require collection of about 99.6 percent of the fluoride evolved from the GTSP production process. This efficiency can be obtained by a two-stage system consisting of a venturi and a spray-crossflow packed bed scrubber.

Rationale

Economic impact of the emission guideline is moderate. Only 25 percent of the industry is directly affected by the emission guideline. The remaining 75 percent will be required to meet more stringent State regulations.

Relaxing the emission guideline by 50 percent would provide greater flexibility with regard to the development of a control strategy, however, it would also allow the emission of an additional 66 tons of fluoride per year. A five-fold increase in the emission guideline would be necessary to allow the use of a venturi or a cyclonic spray tower as the secondary scrubber in all effluent streams.

The estimated retrofit costs (\$666,000 for a 400 ton P_2O_5/day plant) are not considered excessive. Annualized control costs amount to 0.52 percent of sales.

The emission guideline would reduce annnual fluoride emissions from GTSP production facilities by 51 percent.

8.2.6 Granular Triple Superphosphate Storage Facilities

Fluoride Emission Guideline

2.5 X 10^{-4} gram fluoride (as F^-) per hour per kilogram of P_2O_5 in storage.

Discussion

The fluoride emission guideline for existing granular triple superphosphate storage facilities is equal to the SPNSS. In order to meet this emission level, a typical facility would be required to remove approximately 90 percent of the fluorides evolved. Only 25 to 35 percent of the industry currently has this degree of control. Twenty-five percent of the existing facilities are presently uncontrolled.

Rationale

It is estimated that 50 percent of the industry would still be required to add retrofit scrubbers even if the allowable emissions were increased by 50 percent.

The cost of retrofitting uncontrolled facilities would not vary significantly with moderate (50 percent) relaxation of the emission guideline. The major portion of the costs is associated with refurbishing the building and is exclusive of the control device itself.

3. Retrofit costs for uncontrolled facilities ($596,000 for a 25,000 ton storage building) are not considered to be excessive. Such a facility would accompany a 400 ton P_2O_5/day GTSP production facility. Annualized control costs, including capital charges, would equal 0.4 percent of sales.

4. The emission guideline would reduce annual fluoride emissions from GTSP storage facilities by 67 percent.

8.3 REFERENCES

1. Atwood, W. W., Occidental Chemical Company to Goodwin, D. dated June 27, 1973. Fluorine Emissions from Submerged Combustion Evaporation of Phosphoric Acid.

2. Crane, George B. Private communication with Teller Environmental Systems, Inc. New York, N.Y. December 13, 1974.

9. ENVIRONMENTAL ASSESSMENT

9.1 ENVIRONMENTAL ASSESSMENT OF THE EMISSION GUIDELINES

9.1.1 Air

Installation of retrofit controls similar to those described in section 6.1.3.1 could reduce fluoride emissions from existing sources by the amounts indicated in Table 9-1. Emission reductions range from 50 percent for granular triple superphosphate production facilities to 88 percent for run-of-pile triple superphosphate plants. All estimates are based on information presented in chapters 3, 5, and 6 of this study.

The following procedure was used to arrive at the estimates listed in Tables 9-1 and 9-2. The percentage of existing facilities (or capacity) attaining emission levels equivalent to SPNSS was estimated in Chapter 5. The remainder of the existing facilities were assumed to emit at a rate midway between the SPNSS level and a level characteristic of a poorly controlled plant. The retrofit models were used as a source of information regarding poorly controlled plants.

Total emissions following the installation of retrofit controls were estimated by applying the SPNSS level to the entire industry which is identical to the 111(d) emission guidelines contained herein. All estimates assume a 90 percent utilization of production capacity.

This general approach was altered in certain instances (SPA, DAP, GTSP storage) either to make use of additional information or to compensate for the lack of necessary data.

Table 9-1. ANNUAL U.S. FLUORIDE EMISSION REDUCTION DUE TO INSTALLATION OF RETROFIT CONTROLS CAPABLE OF MEETING EMISSION GUIDELINES

Segment of Industry	Estimated 1974 Emissions (Tons F/Yr)	Estimated Emissions Following Installation of Retrofit Controls (Tons F/Yr)	Fluoride Emission Reduction (% 1974 level)
WPPA	217	58	73
SPA	7.7	3.5	55
DAP	251	89	65
ROP-TSP	599	70	88
GTSP			
Production	268	131	51
Storage	119	39	67
Overall	1,462	390	73

Table 9-2. TYPICAL 1974 FLUORIDE EMISSIONS SOURCE STRENGTHS BEFORE AND AFTER INSTALLATION OF RETROFIT CONTROLS CAPABLE OF MEETING EMISSION GUIDELINES

Type of Plant	Capacity (Tons/Day P_2O_5)	Emissions Before Retrofit* (Lb F/hr)	Emissions After Retrofit (Lb F/hr)
WPPA	500	4.8	.42
SPA (Submerged combustion process)	300	.75	.12
DAP	500	5.0	1.25
ROP-TSP	550	89	4.6
GTSP			
Production	400	17.2	3.34
Storage	2000**	4	2

* Based upon those sources that have mediocre control.

** Tons GTSP stored for 5 days.

As indicated in Table 9-1, an overall fluoride emission reduction of nearly 75 percent can be achieved by installation of retrofit controls capable of meeting the emission guidelines. The corresponding reduction in typical fluoride emission source strengths is illustrated by Table 9-2.

9.1.1.1 Atmospheric Dispersion of Fluoride Emissions

A dispersion analysis was made to compare ground-level fluoride concentrations downwind of a phosphate fertilizer complex, before and after retrofit of controls. The diffusion estimates were based on 30-day average fluoride concentrations and extended to distances from the plant where fluoride concentrations were less than 0.5 $\mu g/m^3$. A 30-day average ground-level fluoride concentration of 0.5 $\mu g/m^3$ causes an accumulation of more than 40 ppm fluoride in cattle forage, and this concentration in their feed is a damage threshold for cattle.

The fertilizer complex being investigated represents no actual plant, but contains all of the units discussed in Section 6.1.3.1 - Retrofit Models - except the submerged combustion-superphosphoric acid plant. The model used to calculate emissions from an existing complex after retrofit was assumed to contain an additional new and well-controlled WPPA plant. A railroad spur and WPPA storage facilities were also assumed with which acid could be shipped in or out of the complex. Emissions from this complex are not necessarily typical of the emissions used in the retrofit models of section 6, nor are they the same as the source strengths listed in Table 9-2. However, these emissions fall within the range of emissions from actual plants. Specific

Table 9-3. EXISTING CONTROLS AND EMISSIONS FOR MODEL PHOSPHATE FERTILIZER COMPLEX*

Product	Items Controlled	Gas Flow, SCFM	Fluoride, lbs/hr	Stack		
				height, ft.	temp., °F	gas velocity, ft/sec
WPPA	digester, filter, flash cooler seal tank, evaporator hotwell	21,500	10.8	60	100	30
DAP	reactor-granulator, drier, cooler-screen	110,000	3.3	85	100	30
TSP	cone mixer, den, storage bldg	182,000	26.7	60	90	30
GTSP	-	75,000 from uncontrolled storage bldg	13.2	bldg. louvers @ 45 ft	85	-
	reactor-granulator, drier, cooler-screen	112,000	22.6	85	90	30

* Based on complex not presently meeting guideline emissions.

Table [illegible] RETROFIT CONTROLS AND EMISSIONS FOR MODEL PHOSPHATE FERTILIZER COMPLEX

Product	Items Controlled	Gas Flow, SCFM	Fluoride, lbs/hr	Stack		
				height, ft	temperature, °F	gas velocity ft/sec
WPPA	Table 9-3, plus filtrate sump and seal tank, plus acid storage	25,000	0.42	85	100	40
DAP	same as Table 9-3	96,000	1.25	85	100	30
TSP	same as Table 9-3	182,000	4.54	70	90	30
GTSP	storage building	76,000	2.00	70	85	40
	same as Table 9-3	111,000	3.34	85	90	40

fertilizer manufacturing units are pictured in Figures 6.3, 6.4, and elsewhere. All of these units were assembled to scale on a plot plan of the entire complex. From this plot plan the meteorologist could measure the distance relationships of sources and of interferences such as buildings and phosphate rock piles. The heights of these interferences were also tabulated. Additional information used is shown in Tables 9-3 and 9-4. The former table indicates emissions from the fertilizer complex having existing mediocre emission controls. The latter table shows the emissions from the same sources after installation of good controls. Since the new WPPA facility of the retrofitted complex was considered to meet the emission guidelines, its effect is ignored in Table 9-4.

The source data indicated that aerodynamic downwash was a problem at the facility modeled, particularly for wind speeds in excess of 3 or 4 meters per second. At lower wind speeds, plume rise from some of the stacks could be significant. Plume rise factors were consequently developed, which accounted for the plume rise at low wind speeds and downwash at higher speeds. Those factors were then incorporated into the dispersion estimates.

The dispersion estimates were made through application of the Climatological Dispersion Model (CDM). The CDM provides estimates of long-term pollutant concentrations at selected ground-level receptors. The model uses average emission rates from point and area sources and a joint frequency distribution of wind direction, wind speed, and stability.

One year of monthly stability-wind data from Orlando, Florida were utilized in the CDM dispersion estimates. The climatology of that location is representative of that at facilities of concern in this document. The CDM estimates are typical high 30-day average ambient fluoride concentrations. The results of the analysis are presented in Table 9-5. A more general review of 5-year summaries of monthly stability-wind data from the same location verified that the values presented in Table 9-5 are representative of typical high 30-day average concentrations for any given year.

Table 9-5 shows that the best technology retrofit controls made a large reduction in the ground-level fluoride concentrations which had existed when the mediocre controls were used on the four sources shown. At distances greater than about 1-1/2 mile, the concentrations do not exceed 0.5 μg/m^3, even in the most unfavorable months when the emission guidelines herein are applied.

Table 9-5. ESTIMATED 30-DAY AVERAGE AMBIENT FLUORIDE CONCENTRATIONS DOWNWIND OF A PHOSPHATE FERTILIZER COMPLEX

Fluoride Sources		Estimated 30-Day Average Fluoride Concentration (μg/m^3)					
Existing Controls	After Retrofit	1	2	3	5	10	15 km
WPPA DAP TSP GTSP		6	4	3	1.9	1.0	0.5
	WPPA DAP TSP GTSP	0.8	0.6	0.4	0.3	0.1	0.1

9.1.1.2 Emission Guidelines vs. a Typical Standard

Ten states presently have regulations covering fluoride emissions from fertilizer plants in particular and fluoride emissions in general. Two states, Iowa and Mississippi, limit emissions to 0.4# F/ton P_2O_5 with Montana setting a 0.3# F/ton P_2O_5 limit. Iowa also has a 100 # F/day maximum emission rate. Virginia and North Carolina have variable rates based upon production levels. Four states have regulations based upon ambient concentrations and best control technology. Florida, the state having the most plants, also has the most thorough standard. Table 9-6 gives a comparison of the emission guidelines with the Florida standards. In all cases, the typical standard is as strict or more so than the emission guidelines.

9.1.2 Water Pollution

Increased or decreased control of gaseous water-soluble fluorides will not change the amount of liquid waste generated by the phosphate industry. Most control systems now in use utilize recycled process (gypsum pond) water as the scrubbing medium thereby eliminating the creation of additional effluent. Phosphate fertilizer plants do not need to discharge gypsum pond water continuously. The pond water is re-used in the process, and a discharge is needed only when there is rainfall in excess

Table 9-6. COMPARISON OF EMISSION GUIDELINES AND A STATE STANDARD

Process Source of Fluorides	Percent of Plants Probably Affected by State Guidelines Standard	Florida Standard for July 1, 1975	Emission Guidelines
		lbs/ton P_2O_5 input	
Wet Process Phosphoric Acid	26	0.02	0.02
Superphosphoric Acid	21	Best Available Technology	0.01
Diammonium Phosphate	60	0.06	0.06
Triple Superphosphate (ROP)	40	Belt & Den 0.05 Storage 0.12	0.2
Granular Triple Superphosphate	25	0.15	0.2
Granular Triple Superphosphate Storage	70	0.05**	5×10^{-4}*

*Units are lbs F/hr/ton of P_2O_5 stored.

**Units are lbs F/hr/ton of P_2O_5 input to bldg.

of evaporation.[1] For this reason, the volume of effluent from phosphate fertilizer plants is almost exclusively a function of rainfall conditions. EPA effluent limitations guidelines require that any gypsum pond water discharged to navigable waters when rainfall exceeds evaporation meet the limitations in Table 9-7. A two-stage lime neutralization procedure combined with settling is sufficient control to meet these limitations.

Table 9-7. EPA EFFLUENT LIMITATIONS GUIDELINES FOR GYPSUM POND WATER[1]

Aqueous Waste Constituent	Maximum Daily Concentration (mg/l)	Maximum Average of Daily Values for Periods of Discharge Covering 30 Consecutive Days (mg/l)
Phosphorus as (P)	105	35
Fluoride as (F)	75	25
Total Suspended nonfilterable solids	150	50

The pH of the water discharged shall be within the range of 8.0 to 9.5 at all times.

The phosphate industry has voiced concern that the partial pressure of fluoride out of pond water makes it infeasible in some cases to reach SPNSS fluoride limitations with a scrubber using pond water. An equilibrium fluoride concentration between 5000-6000 ppm seems to be established in gypsum ponds - possibly because of a slow reaction between gypsum and soluble fluosilicates.[2,3,4] Even a pond with an apparent fluoride concentration of 12,500 ppm has fallen within this equilibrium range when the water was passed through a millipore filter.[5] The excess fluoride can be attributed to suspended solids. Pond water containing about 6000 ppm of fluoride has a low enough partial pressure of fluoride to allow scrubber vendors to design to meet emission guidelines. In all cases, emission guidelines can be achieved with pond water if a well-designed spray-crossflow packed bed scrubber is used as the control device.[5]

9.1.3 Solid Waste Disposal

Any solid waste generated by scrubbing fluorides would be in the form of CaF_2 or similar precipitates in the gypsum ponds. The amount of precipitate formed is negligible in comparison to the amount of gypsum generated in producing wet process phosphoric acid, a required intermediate throughout the phosphate fertilizer industry. An example of the relative amounts of each of the solids produced in normal processing with scrubbers which meet emission guidelines for a 500 tons/day P_2O_5 WPPA plant.is presented below:

Assumptions:

1. 6427# phosphate rock = 1 ton P_2O_5.
2. Phosphate rock is 35 weight percent Ca.
3. Uncontrolled emissions of 58.1 #F/hr are reduced to 0.42 #F/hr by a scrubber. (See retrofit model WPPA plant, case B).
4. All of the F absorbed by the scrubber precipitates in the gypsum pond as CaF_2. (See Section 5.2.1, page 5-6).
5. The plant capacity is 500 tons/day P_2O_5.

$3Ca_{10}(PO_4)_6F_2 + 30H_2SO_4 + SiO_2 + 58H_2O \rightarrow 30\ CaSO_4 \cdot 2H_2O$ (4-1)

$+ 18H_3PO_4 + H_2SiF_6$.

This reaction implies: 40#Ca → 172# gypsum.

$$\text{gypsum produced} = \frac{500 \times 6427 \times 0.35 \times 172}{24 \times 40} = 201{,}510\ \text{\# gypsum/hr}$$

From assumptions 3 and 4:

F absorbed in scrubber = 58.1 - 0.42 # F/hr

= 57.68 # F/hr

$$Ca^{++} + 2F^- \rightarrow CaF_2 \downarrow \qquad (5\text{-}1)$$

$$CaF_2 \downarrow = \frac{57.68 \times 78}{38} = 118.4\ \text{\# } CaF_2\text{/hr}$$

$$\%\ \text{increase in solids} = \frac{118.4 \times 100}{201{,}510} = 0.06$$

This example illustrates that the increase in solids due only to scrubbing fluorides is negligible (0.06%). The disposal of the large volume of gypsum is by depositing in mined-out areas, and by lagooning, followed by drying and piling techniques. Such piles are as much as 100 feet above grade in some areas.

9.1.4 Energy

Changes in fluoride control electrical power requirements for the spray-crossflow packed bed scrubber retrofit models in Section 6 are presented in Table 9-8. Existing fluoride control power requirements were estimated from the pump and fan requirements for the assumed existing

Table 9-8. INCREMENTAL POWER REQUIREMENTS FOR FLUORIDE CONTROL DUE TO INSTALLATION OF RETROFIT CONTROLS TO MEET EMISSION GUIDELINES.

Type of Plant	Capacity (Ton/Day P_2O_5)	Power Requirements for Existing Controls (HP)	Power Requirements for Retrofit Controls to Meet State Guidelines (HP)	ΔPower (HP)	Δ Energy (KWH/Ton P_2O_5)
WPPA	500	90	140	50	1.8
SPA	300	75	82.5	7.5	0.4
DAP	500	565	800	235	8.4
ROP-TSP (Case A)	550	300	500	200	6.5
GTSP	400	540	1100	560	25

controls in the retrofit models. Power requirements for the retrofit controls were obtained by adding the power ratings of the specified retrofit fans and pumps to the existing power requirements and subtracting the power for any fans or pumps removed in retrofitting.

The largest incremental power requirement for fluoride control is for GTSP. This can be attributed to installing a spray-crossflow packed bed scrubber for GTSP storage, a previously uncontrolled source in the retrofit model which generates a very large volume of air having a small concentration of fluoride. Raising the standard to allow larger emissions from GTSP storage would not greatly reduce these power requirements. It would only allow the use of a scrubber with a fewer number of transfer units. A less efficient scrubber would not reduce the volume of gas to be scrubbed nor would it greatly reduce the amount of pond water required for scrubbing. Only the pressure drop through the scrubber would be reduced by raising the standard. In other words, raising the GTSP storage standard by a factor of two would not reduce the power requirements proportionately.

Incremental increases in phosphate fertilizer processing energy requirements are given in Table 9-9; such increases will vary from plant to plant. Volumetric flow rates of fluoride-contaminated air sent to the scrubbers can vary by a factor of two or three for the same size and type of plant. Existing control schemes will also influence incremental power requirements by the extent to which their pumping and fan systems can be adapted. Therefore, the numbers presented in Tables 9-8 and 9-9 should be considered approximate.

Fertilizer processing energy requirements presented in Table 9-9 are primarily based upon material in reference (6). The types of energy utilized by the various processes vary. For example, approximately 50 percent of the energy required in GTSP processing can be attributed to the 3 gallons of fuel oil used per ton P_2O_5 processed while nearly all the energy used in the submerged combustion process for SPA comes from natural gas. All processing energy requirements listed in Table 9-9 include electrical power required for rock crushing and pumping.

Table 9-9. INCREASE IN PHOSPHATE INDUSTRY ENERGY REQUIREMENTS RESULTING FROM INSTALLATION OF RETROFIT CONTROLS TO MEET EMISSION GUIDELINES

Fertilizer process	Existing energy requirements (KWH/Ton P_2O_5)	Fluoride control incremental energy requirements (KWH/Ton P_2O_5)	Percent increase in energy requirements
WPPA	225	1.8	0.8
DAP*	236	8.4	3.6
SPA*	782	0.4	0.05
ROP-TSP*	152	6.5	4.3
GTSP*	305	25	8.2

*Existing energy requirements figures include energy needed to process WPPA feed for process.

Annual incremental electrical energy demand for fluoride control is presented in Table 9-10. These figures are based upon Tables 9-6 and 9-8 along with production statistics in section 3. The total incremental

Table 9-10. INCREASED ELECTRICAL ENERGY DEMAND BY THE PHOSPHATE INDUSTRY AS A RESULT OF INSTALLATION OF RETROFIT CONTROLS

Fertilizer Process	1973 Production (Thousand Tons P_2O_5)	% of Production Capacity Affected by State Guidelines Standard	Incremental Electrical** Energy Demand (Million KWH/yr)
WPPA	6,293	26	2.9
DAP	3,312	60	16.7
SPA	783	21	0.06
ROP-TSP	783	40	2.0
GTSP	1,460	47*	17.0

*This is a fictitious average based upon a weighted average of GTSP production and storage statistics (see Table 9-6).

**Total Incremental Electrical Energy Demand = 38.7 $\times 10^6$ KWH/yr (<4 megawatts).

electrical energy demand resulting from installation of retrofit controls to meet emission guidelines is equivalent to the energy required to operate one 300 ton/day P_2O_5 SPA plant 115 days/yr. It should be emphasized that these numbers can be only approximations. As mentioned in the discussion of Tables 9-8 and 9-9, individual plant fluoride control energy and power requirements will vary. This variability necessarily constrains the accuracy of projections based upon single retrofit models.

9.1.5 Other Environmental Concerns

Due to the proposed method of fluoride control, namely, utilization of a spray-crossflow packed bed scrubber with pond water as the scrubbing medium, no other environmental concerns are anticipated. Scrubbing fluorides with gypsum pond water produces a closed system effect for phosphate fertilizer complexes. Although radioactive materials have been detected in the wastewater at fertilizer complexes, recycling of the pond water to the scrubber is not expected to contribute to this potential problem.[7]

9.2 ENVIRONMENTAL IMPACT UNDER ALTERNATIVE EMISSION CONTROL SYSTEMS

Analysis of the data base on which the emission guidelines are based indicates that only the spray-crossflow packed bed scrubber can meet emission guidelines in all cases. ROP-TSP plants can use cyclonic spray tower scrubbers to meet the emission guidelines, but at a higher cost than for a spray-crossflow packed bed scrubber (Table 6-44). Tables 6-37 and 6-40 show that the ROP-TSP standard is the only one substantiated by data which allows use of an alternative scrubber design. Use of either scrubber design for controlling ROP-TSP plants would result in similar environmental impacts. Except for ROP-TSP plants, raising the emission guidelines to allow use of alternative scrubber designs would result in a 50 percent to 1000 percent increase in fluoride emissions without causing any beneficial environmental impacts.

9.3 SOCIO-ECONOMIC IMPACTS

The phosphate fertilizer industry is generally recognized as a capital intensive industry; labor requirements for production work and plant supervision are small, compared to plant sales. Usually, these fertilizer facilities which may be affected by the emission guidelines are widely dispersed throughout the United States. Only in central Florida does the fertilizer industry represent a substantial portion of overall community economic activity and employment, and Florida enacted emission standards effective July 1, 1975 which are at least as strict as the emission guidelines. Therefore, any potential plant closures as a result of the implementation of 111(d) regulations will produce minimal community effects in terms of job losses and sales revenues.

Retrofitting existing plants for controls should not impede new plant construction programs. During the years 1973 through 1974, the phosphate industry entered an expansionary phase with the construction of several new fertilizer manufacturing complexes. The construction rate is expected to decrease after 1976 as these new plants come on-stream. Installation of retrofit controls will consequently occur during a period of slack construction activity and should not interrupt the long-term availability of phosphate fertilizers.

9.5 REFERENCES

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